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THE UNIVERSITY OF ALBERTA

STRUCTURAL AND CHEMICAL INVESTIGATIONS OF ARYLDIAZONIUM AND DIAZOALKANE SPECIES

by

Michele Dorothy Gauthier

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

IN

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EDMONTON, ALBERTA

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THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled STRUCTURAL AND CHEMICAL INVESTIGATIONS OF ARYLDIAZONIUM AND DIAZOALKANE SPECIES submitted by Michele Dorothy Gauthier in partial fulfilment of the requirements for the degree of Master of Science in Chemistry.

Martin Cowie

Wayne F. Reed

Joel Tasker

Date July 25, 1980

To Miles

and my Family

ABSTRACT

The X-ray structural determination of $[(\eta^5\text{-}C_5H_5)_2W\text{-}(NH_2NPh)][BF_4]$, (Ph = (C_6H_5)), has indicated that the coordination about the W atom is pseudotetrahedral, with two of the coordination sites occupied by the cyclopentadienyl rings, and two by the novel side-on bonded phenylhydrazido-(1-) ligand. This unusual ligand has resulted from the insertion of $(C_6H_5)N_2^+$ into both W-H bonds of $[(\eta^5\text{-}C_5H_5)_2\text{-}WH_2]$. The two W-N bond lengths are inequivalent (2.156(9) and 2.034(9) Å), with the shorter distance corresponding to the three-coordinate nitrogen atom, which is bonded to the phenyl group. The N-N distance (1.43(1)Å) corresponds to a normal N-N single bond.

Two diazoalkane molecules, $(PhCO)_2CN_2$ and $PhCOCN_2Ph$ have been structurally characterized. The former, dibenzoyldiazomethane, was found to have an s-trans-s-cis geometry of the carbonyl and diazo groups about the C-C single bonds. This molecule is non-planar, although the structural parameters (N-N = 1.112(2)Å, C-N = 1.339(2)Å, C-O = 1.224(2) and 1.221(2)Å) indicate a significant amount of π-delocalization between the two carbonyl groups and the diazomethane moiety. The carbonyl and diazo groups in the second diazoalkane compound, benzoylphenyldiazomethane, are trans to each, and the molecule, again, is non-planar. As was the case for $(PhCO)_2CN_2$, there is a significant amount of π-delocalization between the carbonyl and diazo groups,

(N-N=1.130(5)Å, C-N=1.328(5)Å, C-O=1.231(4)Å), although there is little conjugation between the phenyl rings and these two groups.

The chemistry of one of the diazoalkane molecules, dibenzoyldiazomethane, with several Rh and Ir complexes has been investigated. In the reaction of $[IrCl(N_2)(PPh_3)_2]$ and $((C_6H_5)CO)_2CN_2$, several species were formed, of which only one compound was characterized - $[IrCl\{(OCPh)_2CN_2\}(PPh_3)_2]$, in which the diazoalkane molecule is chelated through the two ketonic oxygen atoms. No reaction occurred between $[IrCl(CO)(PPh_3)_2]$ and dibenzoyldiazomethane. The reaction of the diazoalkane and $[IrCl(C_8H_{14})_2]_2$ and PPh_3 resulted in the formation of several species, and one of these, $[IrCl((C_6H_4)COCC(Ph)OPPh_2)(PPh_3)_2]$ was structurally characterized. This complex was found to contain the unusual tridentate ligand, $((C_6H_4)COCC(Ph)OPPh_2)$, which is coordinated to the metal through an orthometallated phenyl ring, a vinylic carbon atom and a phosphorus atom, and has been formed through the condensation of the carbene fragment $(PhCO)_2C$ and a diphenylphosphine group. In an analogous reaction between $[IrCl(C_8H_{14})_2]_2$, $(P(i\text{-}C_3H_7)_3)$ and $(PhCO)_2CN_2$, the phosphazine $(i\text{-}C_3H_7)_3P=N_2C(COPh)_2$ was the only product detected, while the reaction of $[RhCl(C_8H_{14})_2]_2$, PPh_3 and the diazoalkane produced two products: a phosphazine, $Ph_3P=N_2C(COPh)_2$, and a phosphorus ylide, $Ph_3P=C(COPh)_2$. If a mixture of $[RhCl(PPh_3)_3]$ and $[RhCl(PPh_3)_2]_2$ were reacted with dibenzoyldiazomethane, only the former reacted, producing the phosphorus ylide, $Ph_3P=C(COPh)_2$.

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ABBREVIATIONS

Ar = aryl

Me = methyl

Ph = phenyl

L = ligand

Et = ethyl

bipy = 2,2'-bipyridine

PPP = $[Ph_2P(CH_2)_3]PPh$

Cy = cyclohexyl

DPM = bis(diphenylphosphino)methane

Bu = butyl

Cp = cyclopentadienyl

CR = centre of ring

CR1 = centre of ring 1

CR2 = centre of ring 2

THF = tetrahydrofuran

Chapter I.

INTRODUCTION

The transition metal chemistry of two closely related species, the aryldiazonium cation (N_2Ar^+) and the diazoalkane molecule (N_2CRR') have been the subject of much interest in recent years.[1,2] Metal complexes of the former species have been used as model systems for the study of nitrogen fixation, whereas the importance of diazoalkane compounds has resulted from their synthetic utility in organometallic chemistry.

Metal-aryldiazonium complexes have been studied in relation to nitrogen fixation, the process in which dinitrogen is reduced to ammonia.[3] Commercially, this process is a key step in the manufacture of plastics and fertilizers, but requires high temperatures and pressures. In nature however, nitrogen fixation is catalyzed in some plants under ambient conditions by nitrogenase, an enzyme containing molybdenum and iron.[4] The industrial importance of an easily synthesized catalyst which could mimic the action of nitrogenase is obvious, and much work is currently underway in attempts to produce such a species. Researchers have used various metal complexes as model systems in these studies, in particular metal-dinitrogen complexes[5] and metal compounds with dinitrogen-containing

ligands.[6] One prime example of the latter is the aryldiazonium cation.

Interest in diazoalkane molecules, on the other hand, has mainly been as a result of their versatility as reagents in the preparative chemistry of transition metal complexes,[2] since a wide variety of metal complexes are formed from aliphatic diazo compounds. Some of these complexes contain the intact diazoalkane molecule, while others contain fragments of the diazoalkane molecule, either intact or rearranged. The complexes formed include alkyl, olefin, acetylene, carbene, ketene, μ-methylene, μ-methylidene, alkylazo, ketenimine and ketazine metal species.[2] The mechanisms for many of the reactions producing these species are unknown and are under investigation.[2] The transition metal coordination of diazoalkane molecules is also relevant to studies involving metal coordinated olefins. Although these latter species have been widely studied in organometallic chemistry,[7] especially in relation to catalysis, the related diazoalkane species containing C=N or N=N bonds are much more uncommon.

In studying the chemistry of transition metal complexes with aryldiazonium and diazoalkane molecules, it is necessary to understand not only the synthetic reactions leading to metal-coordinated species but also the structural details of these species, and their subsequent reactions. There has been a considerable amount of work done in each of

these areas already, and the results to date are briefly presented below.

Metal-diazonium complexes have been synthesized through two major routes,[1] either directly by the reaction of a diazonium salt with a metal compound or indirectly through the reaction of various organic molecules (such as arylhydrazines or diazenes) with metal species. In the direct reactions with diazonium salts, metal-coordinated compounds have been formed through substitution, oxidative addition or insertion reactions followed by deprotonation, as illustrated in equations (1), (2) and (3), respectively.

$$[Na][(Mo(C_5H_5)(CO)_3] + [p\text{-}MeOC_6H_4N_2][BF_4] \longrightarrow$$
$$CO + [Mo(C_5H_5)(CO)_2(p\text{-}N_2C_6H_4OMe)] + [Na][BF_4]\ ^{8} \qquad (1)$$

$$[IrX(CO)(PPh_3)_2] + [ArN_2][BF_4] \longrightarrow$$
$$[IrX(CO)(N_2Ar)(PPh_3)_2][BF_4]\ ^{9} \qquad (2)$$

$X = Cl, Br$

$$[PtHCl(PEt_3)_2] \xrightarrow[EtOH]{ArN_2^+} [PtCl(NHNAr)(PEt_3)_2]^+$$
$$\xrightarrow[-H^+]{base} [PtCl(N_2Ar)(PEt_3)_2]\ ^{10} \qquad (3)$$

Although these direct reactions are straight forward in principle, they are often quite complex, and cannot always be used in the preparation of diazonium complexes. In equation (2), for example, in addition to the product shown,

an orthometallated species $[\overline{Ir(NHNHAr)}(CO)(PPh_3)_2][BF_4]$, a diaryltetrazenido complex $[Ir(N_4Ar_2)(CO)(PPh_3)_2][BF_4]$ and an orthometallated aryldiazene complex $[\overline{IrCl(NHNAr)}(CO)(PPh_3)_2][BF_4]$ were also obtained and characterized.[9]

In the indirect syntheses of metal diazonium complexes, both arylhydrazines (Equation (4)) and aryldiazenes (Equation (5)) have been used.

$$mer\text{-}[ReCl_3(PPhMe_2)_3] + PhNHNH_2 \longrightarrow [ReCl_2(N_2Ph)(PPhMe_2)_3]\ ^{11} \quad (4)$$

$$[Mn(CO)_5Br] + Me_3SiN{=}NPh \longrightarrow [Mn(N_2Ph)(CO)_4]_2 + CO + Me_3SiBr\ ^{12} \quad (5)$$

In addition, metal nitrosyl and metal dinitrogen complexes have been reacted with organic molecules to produce diazonium complexes (Equations (6) and (7), respectively).

$$[Ru(bipy)_2(NO)Cl][PF_6]_2 + RNH_2 \longrightarrow H_2O + [Ru(bipy)_2(N_2R)Cl][PF_6]_2\ ^{13} \quad (6)$$

$$[ReCl(N_2)(PMe_2Ph)_4] + RCOCl \longrightarrow [ReCl_2(N_2COR)(PMe_2Ph)_3] + (PMe_2Ph)\ ^{14} \quad (7)$$

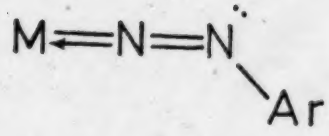
Metal dinitrogen complexes also form diazonium complexes under irradiation in the presence of XR, where X = Cl,Br,I and R = Me, xylene, cyclohexane or ethylformate.[15]

In a reaction with a metal complex, the diazonium ion usually acts as an electrophile through the terminal nitro-

gen atom.[16] Once coordinated, this ligand can display a variety of coordination modes, as shown in Figure 1. The diazonium ion can be terminally bound to one metal centre, or bridging two or more metals. If bound to one metal, the aryldiazonium ligand can act formally as a three-electron donor, or as a one-electron donor. In the former mode, one would expect a linear M-N-N fragment and an NNC angle of approximately 120° (Structure 1a). The ligand in this case is described as being "singly bent" and is formally considered as ArN_2^+.[1] Several such complexes have been synthesized and structurally characterized. In $[Re(N_2Ph)Cl_2(PMe_2Ph)_3]$,[11,17] for example, the M-N-N angle was found to be 173(2)°, while the N-N-C angle was 119(2)°, in agreement with the predicted values. In addition, both the M-N and the N-N bond lengths indicate double bond character (1.77(2) and 1.23(2)Å, respectively), while the N-C bond length (1.43(2)Å) is typical for a single bond between these atoms, as expected for this coordination mode.

As a one-electron donor, the aryldiazonium ligand is doubly bent, with approximately 120° angles about both nitrogen atoms. In this case, the ligand can adopt a trans or cis configuration, as illustrated in Figures 1b and 1c, and is considered formally as ArN_2^-. Three structures have been determined of doubly bent aryldiazonium complexes,[9,18,19] and all have had the trans geometry. A typical example is $[Rh(N_2Ph)Cl(PPP)]^+$,[18] which has an M-N-N angle

Figure 1. Bonding Modes in Metal-Aryldiazonium Complexes.



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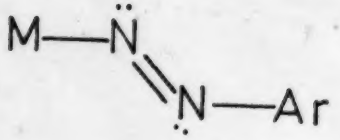

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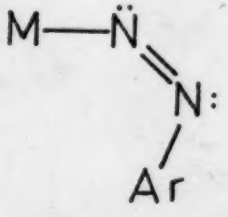

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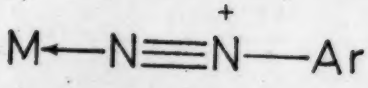

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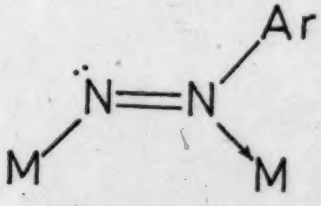

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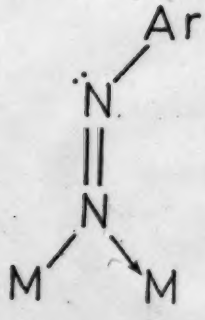


f

of 125.1(6)° and an N-N-C angle of 118.9(8)°. The M-N bond length (1.961(7)Å) is considerably longer than in the singly bent Re complex (described above). The N-N bond length (1.172(9)Å) and the N-C bond length (1.445(11)Å) are in keeping with the double and single bonds expected, respectively, for this geometry.

A complex containing a diazonium ligand with an intermediate geometry, $[IrCl(N_2Ph)(P(CH_3)(Ph_2))_3][PF_6]$, has been reported by Cowie, Haymore and Ibers.[20] In this species the unusual intermediate geometry is attributed to steric crowding about the metal centre, which forces the N_2Ph ligand into the "half doubly bent" configuration. The structural parameters of this ligand confirm the intermediate geometry. Therefore, the M-N-N angle of 155.2(7)° and the M-N bond length (1.835(8)Å) are intermediate between values reported for the singly bent and doubly bent structures. The diazonium ion can be considered as a 2-electron donor in this complex.

The totally linear geometry, as in Figure 1d, has never been structurally characterized although its existence has been postulated for $[RhCl(N_2Ph)(PPh_3)_2][PF_6]$ and $[RhCl(N_2Ph)(CO)(PCy_3)_2]$, where unusually high values of ν_{NN} (1980 and 2000 cm^{-1}, respectively) were observed.[21] The difference between a totally linear configuration and a singly bent geometry is dependent upon the extent of back donation from the metal atom to the diazon-

ium ligand, since very little back donation is expected for the former, and substantial back donation is required for the singly bent geometry.[1] Intermediate back donation from the metal will result in N-N-C angles between the extremes of 120 and 180°, as was observed in $[RuCl_3(p\text{-}N_2C_6H_4Me)(PPh_3)_2]$, where the N-N-C angle is 137.1(5)°.[22]

In addition to bonding through the terminal nitrogen atom to one metal centre, the diazonium ligand can also bridge two metals. Of the two possible geometries shown in Figures 1e and 1f, only the latter has been observed, and three such structures are known, $[Pd_2Cl_2(\mu\text{-}N_2Ph)(DPM)_2]^+$,[23] $[Ir_2(\mu\text{-}O)(\mu\text{-}N_2C_6H_4(2\text{-}NO))(NO)_2(PPh_3)_2][PF_6]$[24] and $[Mn(CO)_4(\mu\text{-}N_2Ph)]_2$.[12] The Mn compound has two bridging diazonium groups, which display similar bonding parameters. Within each ligand, the two M-N bond lengths are virtually identical (2.031(2) and 2.021(2)Å) indicating that the three electrons donated by the diazonium group are equally shared by the two metal centres. The N-N-C bond angle is 119.7(2)°, while the N-N bond length of 1.234(3)Å indicates a double bond and the N-C bond length (1.445(3)Å) is characteristic of a single bond.

Once a metal-diazonium complex is formed, it can undergo a variety of further reactions. Of particular interest to the nitrogen fixation studies, are the protonation reactions of these complexes. In a singly bent aryldiazonium compound, the second nitrogen atom is most likely to be

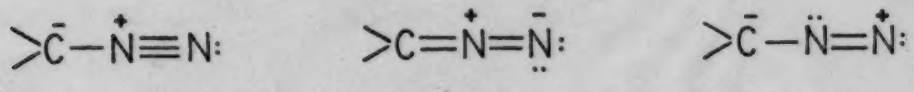
protonated, as was observed for $[ReCl_2(NNHPh)(PMe_2Ph)_2(NH_3)]^+$.[17] On the other hand, with doubly bent aryldiazonium complexes, the site of protonation is the first nitrogen atom, which is bound to the metal. An example of this is the reversible reaction of $[Pt(N_2C_6H_4X)(PPh_3)_3]Y$ [25] (X = *p*-NO_2,F,H,OMe,Me,NEt_2 or NMe_2; Y = BF_4 or BPh_4) with non-coordinating acids to yield $[Pt(NHNC_6H_4X)(PPh_3)_3]^{2+}$.

Hydrogenation studies on metal-diazonium complexes have also been investigated.[26] Singly bent diazonium complexes are not usually hydrogenated under mild conditions,[26] but several doubly bent aryldiazonium species have been hydrogenated under mild conditions in the presence of a catalyst to yield hydrazine complexes ($M\text{-}NH_2NHAr$).[26] Doubly bent aryldiazonium complexes, already protonated on the first nitrogen atom, also react with H_2 to form metal hydrazines.[26] In addition, orthometallated aryldiazonium complexes are readily hydrogenated under mild catalytic conditions, yielding orthometallated arylhydrazine species.[26] In contrast, it has been reported[25] that $[Pt(N_2C_6H_4X)(PPh_3)_3]^+$ complexes (X = *p*-NO,F,H, OMe,Me,NEt_2 or NMe_2) react with H_2 in the absence of a catalyst to produce only N_2 and $[PtH(PPh_3)_3]^+$; no intermediate aryldiazine or hydrazine complexes were observed.

Metal-aryldiazonium complexes may also undergo orthometallation, displacement or oxidative addition reactions. Orthometallation of the aryl group has been observed upon refluxing[27] or if an α-hydridic alcohol, such as ethanol,

is present.[1] In displacement reactions, either the aryldiazonium ligand or another ligand within the complex may be displaced. The former has been observed in the reaction of $[Os(CO)_2(NNPh)(PPh_3)_2]^+$ with BH_4^- yielding $[OsH_2(CO)_2(PPh_3)_2]$,[28] while an example of displacement of another ligand occurs in the reaction of $[PtCl(N_2Ar)(PEt_3)_2]$ with L(L = NH_3, pyridine, PEt_3, EtNC) producing $[PtL(N_2Ar)(PEt_3)_2]^+$, an unstable complex which subsequently decomposes to $[PtL(Ar)(PEt_3)_2]^+$ and N_2.[29] Oxidative addition reactions have also been noted for several metal-aryldiazonium complexes, as in the reaction of $[IrCl(N_2Ar)(PPh_3)_2]^+$ with CO, PR_3, AsR_3, SbR_3 and RCN to form five coordinate species.[30]

Unlike diazonium ions, neutral diazoalkane molecules rarely produce complexes containing the intact molecule in reactions with metal species.[2] This is a function of the electronic structure of diazoalkane molecules, which can be represented by three canonical forms,



a b c

The aliphatic diazo molecules can react as nucleophiles through either the carbon atom (a) or the terminal nitrogen (b); as a 1,3-dipole as in (c); or as a π-donor through either the C-N or N-N moieties.[16] These reaction pathways lead to

three major classes of products: rearranged organic compounds, metal-carbene complexes and metal-diazoalkane complexes.

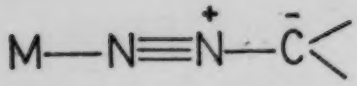
Various organic compounds have been produced from reactions between diazoalkane molecules and metal species. These include ketenes ($RR'C{=}C{=}O$), which have been formed either with an excess of $Ni(CO)_4$ [31] or with catalytic amounts of Cu powder or Ag compounds;[32] methylene addition products, as in the formation of dicyclopropylmethane from cis-$(\eta^3$-allyl$)_2Ni$;[33] polymethylene, produced from reactions between diazomethane and nickelocene[34] or $IrCl(CO)(PPh_3)_2$, (in $CHCl_3$ or benzene);[35] and ethylene, produced from diazomethane and $IrCl(CO)(PPh_3)_2$ in diethyl ether,[35] or $TiCl_4$.[36] Diazoalkanes have also been used in catalytic amounts as initiators in the WCl_6-catalyzed olefin metathesis of cycloalkenes to polyalkenamers of high molecular weight.[37] For most of these products, the reaction mechanisms are not well understood, although it is postulated that primary adducts of the diazoalkane molecule and unstable carbene complexes are involved.[2]

Several metal-carbene products have been isolated from aliphatic diazo molecules. One example is $[(\eta^5\text{-}C_5H_4R)Mn(CO)_2((C_6H_5)CCO(C_6H_5)]$, (R = H,Me) produced from the reaction of benzoylphenyldiazomethane and $[(\eta^5\text{-}C_5H_4R)Mn(CO)_2(THF)]$.[38] This carbene complex produces the corresponding Mn-ketene complex $[(\eta^5\text{-}C_5H_4R)Mn(CO)_2(Ph_2C{=}C{=}O)]$ under

irradiation. Intramolecular rearrangements often occur with these metal carbene complexes. In the reaction of the above Mn-(THF) adduct with 3-diazo-2-butanone for example, the carbene complex cannot be isolated, and the resulting complex, $[(\eta^5\text{-}C_5H_4R)Mn(CO)_2(H_2C{=}CHCOCH_3)]$, an η^2-bound olefin complex, is obtained instead.[38b] Carbenes bridging two metal centres, μ-methylene complexes, have been reported for reactions between diazoalkanes and various metal species, including Mn, Os, Co and Rh.[2] A μ_3-methylidine cluster was also noted from the reaction of diazomethane and $H_2Os_3(CO)_{10}$.[39] Insertion of carbenes produced from aliphatic diazo molecules into metal hydrides has resulted in metal-alkyl compounds, as in the reaction of $(\eta^5\text{-}C_5H_5)Mo(CO)_3H$ with diazomethane to produce $(\eta^5\text{-}C_5H_5)Mo(CH_3)(CO)_3$.[40] Diazoalkane-produced carbenes have also inserted into M-C bonds, which in the reaction of $(\eta^5\text{-}C_5H_5)Co(Ph\text{-}C{\equiv}C\text{-}Ph)(PPh_3)$ and $N_2CH(CO_2CH_3)$, resulted in the formation of three complexes - a mononuclear butadiene, and two bridging hexadiene species.[41]

Relatively few stable metal-diazoalkane complexes have been isolated. This is due mainly to the reactivity of these metal species, which usually results in further reactions and rearrangements (*vide supra*). Within a mononuclear diazoalkane complex, there are several possible bonding modes, and these are presented in Figure 2. In type 2a the diazoalkane molecule is coordinated through the terminal nitrogen atom, and has been observed for such complexes as

Figure 2. Bonding Modes in Mononuclear Metal-Diazoalkane Complexes.



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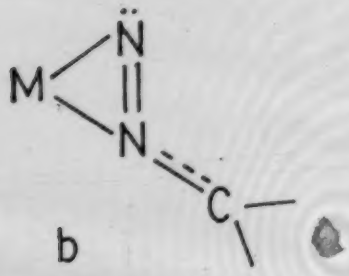

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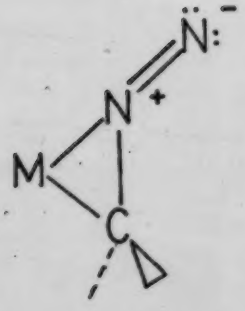

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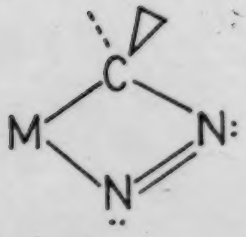

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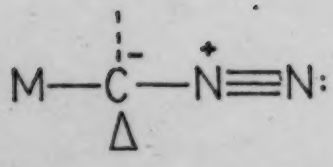

e

$[(\eta^5\text{-}C_5H_5)Mn(CO)_2(N_2C(CO_2C_2H_5)_2)]$,[42] $[IrCl(N_2C_5Cl_4)(PPh_3)_2]$[43] and $[RuH_2(N_2B_{10}H_8S(CH_3)_2)(PPh_3)_3]$.[44] The latter two species have been confirmed by X-ray crystallography. In the iridium complex, the diazoalkane ligand is comparable to the singly bent aryldiazonium ligand in $[IrCl(N_2Ph)(PPh_3)_2]^+$,[30] although the bonding parameters indicate that there is less π-back bonding from the metal to the ligand for the diazoalkane complex (diazoalkane[aryldiazonium] parameters:[43] <Ir-N-N = 174.6(6)°[176.1°], <N-N-C = 141.2(7)°[124.8°], Ir-N = 1.824(6)Å[1.794 Å], N-N = 1.163(7)Å[1.159 Å]). The above ruthenium-diazoalkane complex was found to be totally linear[44] with an M-N-N angle of 175.9(6)° and an N-N-B angle of 172.7(8)°. Analogous linear aryldiazonium complexes have been proposed, although none has been structurally characterized. The Ru-N bond distance (1.889(8)Å) and the N-N bond length (1.115(8)Å) are comparable to those found in ruthenium-dinitrogen complexes.

Diazoalkane complexes coordinated through the N=N double bond (Figure 2b) have been isolated for various metal species, and one such complex, [Ni(*t*-BuNC)$_2$(diazofluorene)] has been structurally characterized.[45] The diazoalkane ligand is bound unsymmetrically to the metal atom, with Ni-N distances of 1.874(3) and 1.834(3)Å. The N-N distance of 1.245(4)Å is characteristic of an N=N double bond and the N-N-C bond angle is 133.8(3)°. Analogous π-coordinated aryldiazonium species have not been observed.

Other coordination modes have been postulated as intermediates in various reactions between metal complexes and diazoalkane molecules, but have not been fully characterized. For example, diazoalkane complexes which are π-coordinated through the N-C bond (Figure 2c) have not been isolated, but may be involved in reactions where the N-N bond is cleaved, as in the formation of ketimine complexes from diazoalkanes.[46] Four-membered metallocycles (Figure 2d) have been suggested as intermediates in the formation of carbene addition products,[47] and this coordination mode has been postulated for $[IrCl(NNC(CF_3)_2)(PPh_3)_2]$,[48] although this has not been confirmed through a structure analysis. Similarly, coordination through the aliphatic carbon atom of the diazoalkane, (Figure 2e) has been considered for primary adducts in several reactions, but compounds with this coordination mode have not been isolated.[2] On the other hand, the related species, containing a metallated diazoalkane, has been reported for several group IB[49] and IIB[50] transition metals, such as $Hg(C(N_2)R)_2$. Metallated diazoalkane complexes of the group VIII transition metals such as $[PdCl(C(N_2)R)(PR'_3)_2]$ and $[Pd(C(N_2)R)_2(PR'_3)_2]$ have been prepared through the reaction of $Hg(C(N_2)R)_2$ with $[PdCl_2(PR'_3)_2]$, where $R = CO_2Et$, C(O)Me, Ph and $R' = Ph, Et$.[51] The X-ray structure of one of the products, $[PdCl(C(N_2)CO_2Et)(PPh_3)_2]$, confirmed the metallated configuration of the diazoalkane ligand.[51]

Metal diazoalkane complexes in which the aliphatic diazo ligand is coordinated to more than one metal centre are very rare. In one reported complex, $[(\eta^5\text{-}C_5H_5)Co]_3(\mu_3\text{-}CO)(\mu_3\text{-}N_2CPh_2)$,[52] the diazoalkane is bridging three cobalt atoms through the terminal nitrogen atom. In $[Mn(CO)_4]_3(\mu_3\text{-}N_2CH_3)$[53] the terminal nitrogen atom is bound to two Mn atoms, while the other nitrogen atom is coordinated to the third Mn centre.

In some reactions, metal-nitrogen species are formed which are not diazoalkane complexes. An illustration of this are the alkyldiazo insertion products $[(\eta^5\text{-}C_5H_5)M(CO)_2(N_2CHRR')]$ where M = Mo,W and R,R' = H,CH_3, $Si(CH_3)_3$, C_6H_5, which are formed from the reaction of $[(\eta^5C_5H_5)M(CO)_3H]$ and N_2CRR'.[54] Another example is the reaction of ethyldiazoacetate with $[Ru(NH_3)_5(H_2O)]^{2+}$ which produces the dinitrogen complexes $[Ru(NH_3)_5(N_2)]^{2+}$ and $[(NH_3)_5Ru\text{-}(N_2)\text{-}Ru(NH_3)_5]^{4+}$.[55]

Some further reactions have been reported for metal-diazoalkane complexes, however, the work done in this area has been limited since so few of the diazoalkane complexes are stable. Schramm and Ibers[43] reported that $[IrCl(N_2C_5Cl_4)(PPh_3)_2]$ oxidatively adds various molecules, such as PR_3, CO, NO^+ and N_2Ph^+, in a manner similar to the addition reactions of the corresponding aryldiazonium complex.[30] Differences however arise between the diazoalkane and aryldiazonium complexes, since the diazoalkane ligand is neutral whereas the diazonium ion is positively charged. Displacement reactions have also been observed with metal-

diazoalkane compounds. The π-coordinated diazofluorene molecule is displaced in the reaction of [Ni(*t*-BuNC)$_2$-(diazofluorene)] with PPh_3, while in the analogous Pd complex, a (*t*-BuNC) group is displaced.[45] In addition, in virtually all metal-diazoalkane complexes, thermal decomposition readily occurs, with loss of the diazoalkane ligand.[2]

The chemistry of diazoalkane molecules with transition metal compounds is very complex, and a wide variety of species, both organic and organometallic, are obtained. This variety, in fact, is the basis for the synthetic utility of diazoalkane molecules in organometallic chemistry. As in the case of the diazonium ions, the mechanisms involved in these reactions are not well understood and there is still much work to be done in this area.

As can be seen , diazoalkane molecules and aryldiazonium ions are closely related, yet their reactions with transition metal compounds are quite different, as are the coordination modes and chemistry of the resultant complexes. This study was undertaken to further investigate the nature of aryldiazonium and diazoalkane transition metal complexes, with particular emphasis on the structural details of the complexes. The technique of X-ray diffraction was used extensively during this study and detailed discussions of the theoretical and experimental considerations of this technique are available in several reference texts.[56-59]

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Chapter II.

The Structure of $[(\eta^5\text{-}C_5H_5)_2W(H_2NNC_6H_5)][BF_4]$: A Complex Containing the Unusual Side-On Bonded Phenylhydrazido(1-) Ligand.

INTRODUCTION

The insertion reactions of aryldiazonium cations into transition metal-hydride bonds have received much attention,[1-3] owing in part to the possible relevance of such studies to the biological reduction of dinitrogen, as initially suggested by Parshall.[4] Although several examples of monoinsertion reactions, in which an aryldiazonium cation inserts into one metal hydride bond, have been characterized and reported,[1-3] the isolation and characterization of stable products resulting from the double insertion of N_2Ph^+ into two metal-hydride bonds had not been reported until recently.[5,6] The hydrazido(1-) species resulting from this double insertion reaction represents an important intermediate in model system studies of dinitrogen reduction.

The reaction of Cp_2WH_2 with N_2Ph^+ at low temperature initially yields[5,6] the monoinserted species, $[Cp_2WH(NNHPh)]^+$, which has been shown to contain a hydrazido(2-) ligand, in which the hydrogen atom is bonded to the second nitrogen atom, remote from the metal.[7] At room temperature this unstable intermediate rearranges to the diinserted

product, $[Cp_2W(H_2NNPh)]^+$, which based on spectral measurements was believed to contain the novel side-on bonded phenylhydrazido(1-) ligand.[5,6] Since the mode of coordination of the hydrazido(1-) ligand in such a complex is of interest in order to gain information related to the stereochemical processes occurring during dinitrogen reduction, the structure of the above hydrazido(1-) complex, as the BF_4^- salt, was undertaken in order to confirm this highly unusual bonding mode.

EXPERIMENTAL

Deep red crystals of the title compound were kindly supplied by Professor Sutton of Simon Fraser University. Preliminary film data showed Laué symmetry 2/m, indicating a monoclinic system. The systematic absences ($h0\ell$, $\ell = 2n+1$ and $0k0$, $k = 2n+1$) uniquely defined the space group as $P2_1/c$. Accurate cell parameters were obtained by a least squares analysis of 12 accurately centered reflections, chosen from diverse regions of reciprocal space ($50° \leq 2\theta \leq 75°$, Cu Kα X-radiation) and obtained using a narrow X-ray source. Table 1 contains the pertinent crystal data.

Data were collected by the θ-2θ scan method on a Picker four-circle automated diffractometer, equipped with a scintillation counter and pulse height analyzer tuned to accept 90% of the Cu Kα peak. Background counts were measured at

Table 1. Summary of Data and Intensity Collection for $[(\eta^5\text{-}C_5H_5)_2W(NH_2NPh)][BF_4]$.

Compound	$[(\eta^5\text{-}C_5H_5)_2W(NH_2NPh)][BF_4]$
Formula Weight	507.98
Formula	$C_{16}H_{17}B_1F_4N_2W_1$
Cell Parameters	
a	8.5874(6)
b	10.4821(8)
c	19.5455(14)
β	107.176(6)
V	1680.9
Z	4
Density	2.007 $g \cdot cm^{-3}$ (calcd.) 2.01(1) $g \cdot cm^{-3}$ (exptl, floatation)
Space Group	C_{2h}^5 - $P2_1/c$
Crystal Dimensions	0.231 x 0.158 x 0.180 mm
Crystal volume	0.00359 mm^3
Crystal Faces (and distances from an arbitrary origin within the crystal (mm))	1 0 0 0.069 1 0 -2 0.132 -2 -1 -6 0.080 -1 0 -1 0.060 -1 0 2 0.032 0 0 1 0.050 0 3 -1 0.125 0 1 1 0.093 0 -1 -1 0.110 0 -1 1 0.088
Temperature	20°C
Radiation	Cu Kα (λ = 1.540562 Å)
μ	132.74 cm^{-1}
Range in Absorption Correction Factors	0.171 - 0.329

Table 1, Continued

Receiving Aperture	3.4 mm wide x 5.2 mm high, 30 cm from the crystal
Takeoff Angle	3.0°
Scan Speed	2° in 2θ/min
Scan Range	0.80° below $K\alpha_1$ to 0.80° above $K\alpha_2$
Background Counting Time	$2\theta \leq 99.00°$, 20s; $2\theta > 99.00°$, 40s
2θ Limits	3.0° - 120.0°
2θ Limits for Centered Reflections	50.0° - 70.0°

Refinement Information

Unique Data Collected	2789
Unique Data Used	1972
Model 1	(Cp Rings Treated as Hindered Rotors)
Final Number of Parameters Varied	149
Error in Observation of Unit Weight	1.736 electrons
R	0.048
R_w	0.064
Model 2	(Cp Rings Treated as Individual Anisotropic Atoms)
Final number of Parameters Varied	225
Error in Observation of Unit Weight	1.640 electrons
R	0.045
R_w	0.057

both ends of the scan range with both crystal and counter stationary. The intensity of the peak (I), assuming approximate linearity of background, is given by

$$I = PK - (B_1+B_2)t_p/t_B \qquad (1)$$

where PK = peak count, t_p = peak scan time, t_B = the sum of the two background collection times and B_1 and B_2 are the background counts. Standard deviations in the intensities were calculated from equation (2):

$$\sigma(I) = (PK+t^2BT+p^2I^2)^{\frac{1}{2}} \qquad (2)$$

where $BT = B_1+B_2$, $t = t_p/t_B$ and p is an ignorance factor, which takes into account machine uncertainty and prevents an unreasonably high weighting being applied to reflections of high intensity.[8] A value of 0.05 was used for p. The intensities of three standard reflections were measured every 100 reflections and were found to decrease by approximately 4% over the duration of the data collection. The observed intensities were corrected for this apparent decomposition.

The intensities of 2789 unique reflections ($3° \leq 2\theta \leq 120°$) were measured using Cu Kα X-radiation. A total of 1972 reflections had $F_o^2 \geq 3\sigma(F_o^2)$ and were used in subsequent calculations. The data were reduced to structure factor amplitudes and standard deviations in the structure factors ($\sigma(F)$) by correction for Lorentz, polarization and absorp-

tion effects.[9-12] Similar procedures for data collection and reduction were followed on all subsequent structures.

STRUCTURE SOLUTION AND REFINEMENT

A Patterson map[13,14] was computed between the limits $0.0 \leq u \leq 1.0$, $0.0 \leq v \leq 0.5$, $0.0 \leq w \leq 0.5$. The W-W vectors for the general position solution of the space group $P_{2_1/c}$ are derived in Table 2. The origin peak in the Patterson map corresponds to the sum of the vectors between every atom and itself in the unit cell, and is roughly proportional to $\Sigma_i z_i^2$, summed over the contents of the unit cell (*i.e.* $4 \times 74^2 + 16 \times 9^2 + 4 \times 5^2 + 8 \times 7^2 + 64 \times 6^2 + 68 \times 1^2 = 26064$). This peak is normalized to 1000 in the Fourier program used to calculate the vector map. Assuming comparable thermal parameters for all atoms, one expects the doubly weighted W-W vectors (see Table 2) to have an approximate, normalized value of 420 (*i.e.* $2 \times 74^2/26064 \times 1000$), and the singly weighted W-W vectors to have a value of 210. The top three peaks after the origin peak in the Patterson map correspond to the W-W vectors, and are listed with their assignments in Table 3. The weights of the next vectors start at 74, and correspond to W-C and W-N vectors. The W-W vectors are considerably stronger than the other vectors in the Patterson map, since the tungsten atom is so heavy compared to the other atoms in the unit cell. As a consequence, the Patterson map is quite useful in solving this structure,

Table 2. Derivation of the W-W Vectors for the Space Group $P2_1/c$.

	x,y,z	$\bar{x},\bar{y},\bar{z}$	$\bar{x},\frac{1}{2}+y,\frac{1}{2}-z$	$x,\frac{1}{2}-y,\frac{1}{2}+z$
x,y,z	0,0,0	2x,2y,2z	$2x,\frac{1}{2},\frac{1}{2}+2z$	$0,\frac{1}{2}+2y,\frac{1}{2}$
$\bar{x},\bar{y},\bar{z}$	$2\bar{x},2\bar{y},2\bar{z}$	0,0,0	$0,\frac{1}{2}-2y,\frac{1}{2}$	$2\bar{x},\frac{1}{2},\frac{1}{2}-2z$
$\bar{x},\frac{1}{2}+y,\frac{1}{2}-z$	$2\bar{x},\frac{1}{2},\frac{1}{2}-2z$	$0,\frac{1}{2}+2y,\frac{1}{2}$	0,0,0	$2\bar{x},2y,2\bar{z}$
$x,\frac{1}{2}-y,\frac{1}{2}+z$	$0,\frac{1}{2}-2y,\frac{1}{2}$	$2x,\frac{1}{2},\frac{1}{2}+2z$	$2x,2\bar{y},2z$	0,0,0

Vectors	Weights
0,0,0	4
$2\underline{x},\frac{1}{2},\frac{1}{2}+2z$	2
$2\bar{x},\frac{1}{2},\frac{1}{2}-2z$	2
$0,\frac{1}{2}+2y,\frac{1}{2}$	2
$0,\frac{1}{2}-2y,\frac{1}{2}$	2
$2\underline{x},2y,2z$	1
$2\bar{x},2\bar{y},2\bar{z}$	1
$2x,2\bar{y},2z$	1
$2\bar{x},2y,2\bar{z}$	1

Table 3. Assignment of the Most Intense Patterson Map Vectors.

No.	u	v	w	Relative Weight	Assignment
1	0.000	0.037	0.500	408	$0, \frac{1}{2}+2y, \frac{1}{2}$
2	0.092	0.518	0.260	356	$2x, \frac{1}{2}, \frac{1}{2}+2z$
3	0.920	0.444	0.240	216	$2\bar{x}, 2\bar{y}, 2\bar{z}$

since the W-W vectors are unambiguous. Based on the vector assignment, the W position (0.05,0.27,0.38) was obtained and input into a full-matrix, least-squares refinement, which converged in 3 cycles to $R = 0.219$ and $R_w = 0.257$. The R values are defined as

$$R = \Sigma||F_o|-|F_c||/\Sigma|F_o| \quad (3)$$

and

$$R_w = \{\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2\}^{\frac{1}{2}} \quad (4)$$

where $|F_o|$ and $|F_c|$ are the absolute values of the observed and calculated structure factors, respectively, and w, the weighting factor, is defined as $w = 1/\sigma^2(F)$. In the least squares refinement the function $\Sigma w(|F_o|-|F_c|)^2$ is minimized. Structure factors were calculated using the atomic scattering factors taken from Cromer and Waber's tabulation[15] for all atoms except hydrogen, for which the values of Stewart *et al.*[16] were used. Anomalous dispersion terms[17,18] for W were included in F_c.

An electron density difference map, phased on the W position yielded the position of all non-hydrogen atoms in the cation. The BF_4^- anion was found after the next least-squares refinement and electron density difference map. The data were corrected for absorption effects by Gaussian integration.

The cyclopentadienyl carbons were refined by two different techniques. In the first method, the carbon atoms

of these rings were treated as hindered rotor groups[19] with D_{5h} symmetry. The positions, orientations, and the radii of these groups and their barriers to libration perpendicular to their group planes were refined. This refinement method has the important advantage over individual atom treatments that more chemically reasonable C-C distances for the Cp rings are obtained. Furthermore, significantly fewer parameters are refined using this technique (see Table 1). In the second method the cyclopentadienyl carbon atoms were refined as individual anisotropic atoms, where the form of the thermal ellipsoid used was $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + 2\beta_{12}hk + 2\beta_{13}h\ell + 2\beta_{23}k\ell)]$. The converged refinements for both models are briefly compared (*vide infra*), however, in spite of the advantages of the rigid body refinement only the individual atom refinement is reported in detail owing to the better standard deviations in the parameters of interest obtained by using this model. In both refinement techniques, the phenyl and cyclopentadienyl hydrogen atoms were included as fixed contributions in the final few least squares refinements. The idealized positions of the phenyl hydrogen atoms were calculated from the geometries about the attached carbon atom using a C-H distance of 0.95 Å. These hydrogen atoms were given isotropic thermal parameters of 1 Å^2 greater than the equivalent isotropic B of their attached carbon atoms. The cyclopentadienyl hydrogen atoms were included as hindered

rotor groups in both refinement methods using the group parameters obtained from the previous hindered rotor refinement of the Cp carbon atoms. The group thermal parameters were set at 1 $\mathring{A}^2$ greater than those of the corresponding carbon atom group. The remaining non-hydrogen atoms were refined individually with anisotropic thermal parameters, while the two hydrogen atoms on N(1) were refined individually with isotropic thermal parameters. The final model, with individual anisotropic Cp carbon atoms, converged at $R = 0.045$ and $R_w = 0.057$ for 225 variables. In the final electron density difference map, the highest 20 residuals (0.03 to 0.90 $e/\mathring{A}^3$) were in the vicinities of the W atom and the BF_4^- anion. A typical carbon atom on earlier Fourier maps had an intensity of approximately 4.00 $e/\mathring{A}^3$. Some difficulty was encountered in refining the BF_4^- anion owing to disorder of this group. More sophisticated models describing this disorder were not used, however, since the four fluorine positions used were clearly the most obvious from difference Fourier calculations (peaks from 2.5 - 5.4 $e/\mathring{A}^3$). In addition, the added effort was not judged worthwhile as no change in the parameters of interest was anticipated; certainly there was no significant change in these parameters between the refinements before and after inclusion of the anion.

The programs used in the solution and refinement of the structure, and presentation of data are listed briefly in Appendix I.

RESULTS

A stereoview of the unit cell is shown in Figure 3. The crystallographic *a* axis is going into the page, the *b* axis is from left to right, and the *c* axis is from top to bottom. In this and all subsequent diagrams unless otherwise noted, vibrational ellipsoids of 20% are shown for all atoms, except hydrogens which are shown artificially small. Figure 4 shows a perspective view of the cation, including the numbering scheme used (phenyl hydrogen atoms have the same number as their attached carbon atom) and some relevant bond lengths. The representation of the cation shown in Figure 5 and viewed in the W-N(1)-N(2) plane, shows the orientation of the phenyl ring in relation to the W-N(1)-N(2) plane and the Cp planes. The final positional and thermal parameters for the non-group atoms are given in Table 4. The idealized positional and thermal parameters for the hydrogen atoms are given in Table 5. Selected interatomic distances and angles are listed in Tables 6 and 7, respectively, while least squares plane calculations are in Table 8. A listing of the observed and calculated structure factor amplitudes is available.[20]

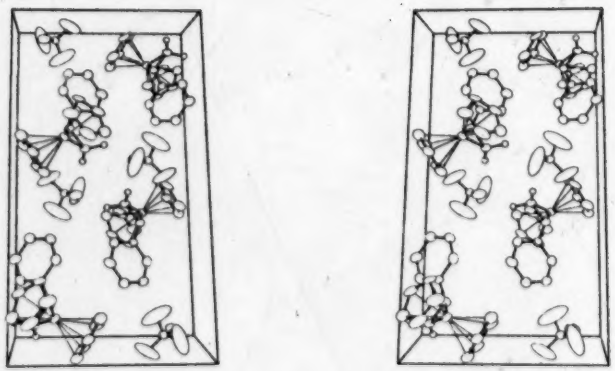

Figure 3. Cell Packing Diagram of $[(\eta^5\text{-}C_5H_5)_2W(H_2NNPh)][BF_4]$.

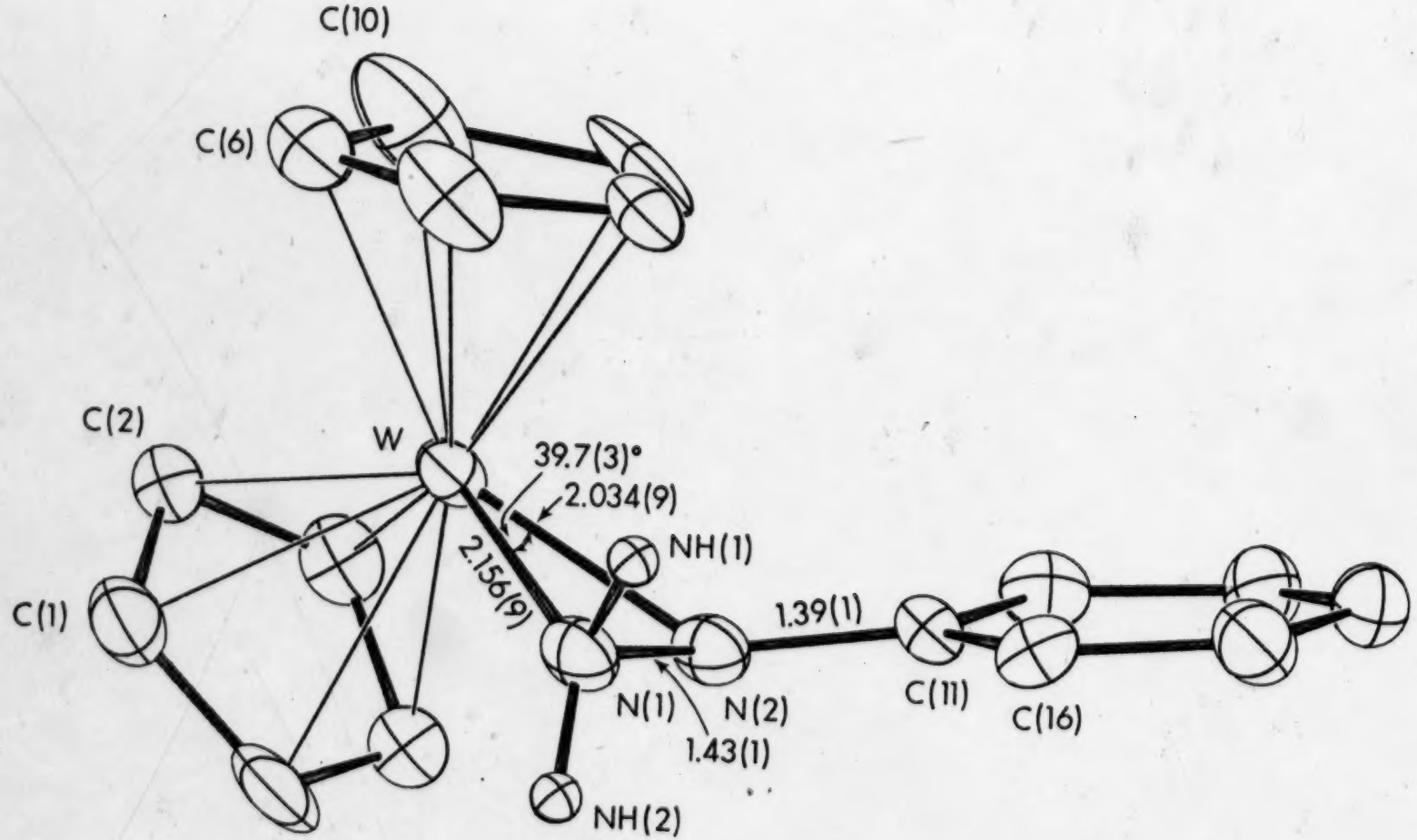

Figure 4. Perspective View of the $[(\eta^5\text{-}C_6H_5)_2W(H_2NNPh)]^+$ Cation.

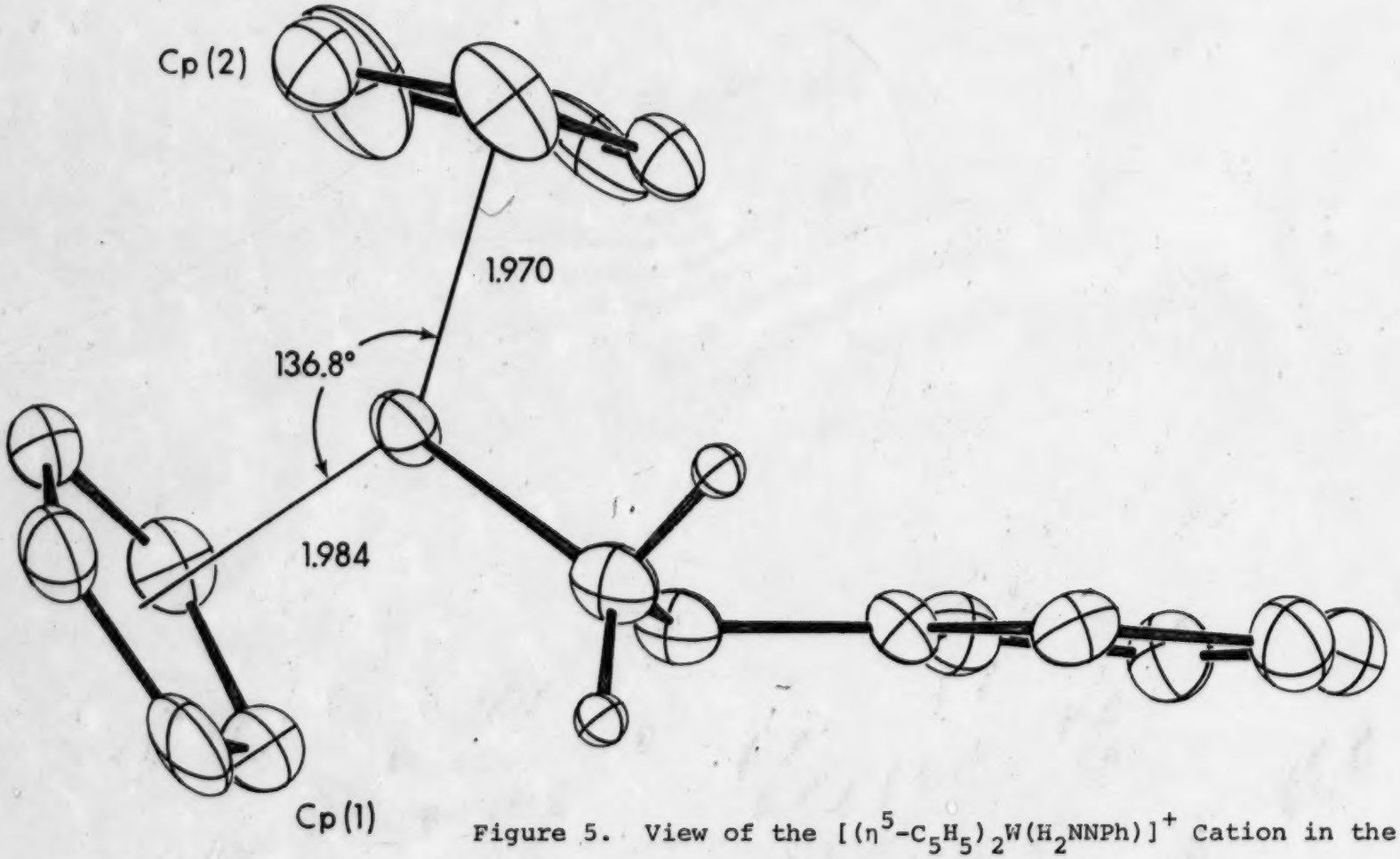

Figure 5. View of the $[(\eta^5\text{-}C_5H_5)_2W(H_2NNPh)]^+$ Cation in the Plane of W-N(1)-N(2).

Table 4. Positional and Thermal Parameters For the Non-Hydrogen Atoms of [Cp2W(NH2NPh)][BF4].

Atom	x[a]	y	z	U11[b]	U22	U33	U12	U13	U23
W	0.04371(6)	0.27560(5)	0.38366(2)	6.00(3)	6.14(3)	6.00(3)	0.50(2)	0.57(2)	0.95(2)
N(1)	0.266(1)	0.385(1)	0.4153(5)	7.2(6)	7.8(7)	6.3(5)	0.2(5)	0.3(4)	-0.4(5)
N(2)	0.252(1)	0.3023(8)	0.3557(4)	7.7(5)	6.8(6)	5.9(5)	0.2(4)	0.7(4)	-0.4(4)
C(1)	0.044(2)	0.171(1)	0.4859(6)	11(1)	9.4(9)	7.3(7)	-0.7(8)	2.4(7)	1.9(7)
C(2)	-0.082(2)	0.118(1)	0.4293(7)	9.4(8)	7.0(8)	10.0(9)	-0.2(7)	3.1(7)	2.0(7)
C(3)	-0.014(2)	0.058(2)	0.3810(8)	11(1)	9(1)	10(1)	0.6(8)	3.4(9)	1.3(8)
C(4)	0.154(2)	0.069(1)	0.407(1)	10(1)	8(1)	15(1)	3.1(8)	5(1)	4.0(9)
C(5)	0.192(2)	0.138(2)	0.4728(8)	7.9(8)	10(1)	11(1)	0.7(7)	0.6(8)	5.9(9)
C(6)	-0.187(2)	0.390(3)	0.379(1)	10(1)	15(2)	15(2)	6(1)	6(1)	7(1)
C(7)	-0.079(2)	0.476(2)	0.372(1)	11(1)	7(1)	15(2)	4.0(9)	0(1)	-0.9(9)
C(8)	-0.039(2)	0.446(2)	0.311(1)	10(1)	9(1)	12(1)	3.3(9)	2(1)	4.7(9)
C(9)	-0.123(3)	0.348(2)	0.2774(7)	13(1)	17(2)	6.9(8)	7(1)	-2.7(9)	-0(1)
C(10)	-0.225(2)	0.308(2)	0.323(2)	5.7(8)	11(2)	25(3)	-0.7(8)	-4(1)	4(2)
C(11)	0.302(1)	0.345(1)	0.2982(5)	5.3(5)	6.1(7)	5.7(5)	1.1(4)	1.0(4)	0.3(5)
C(12)	0.260(2)	0.270(1)	0.2373(7)	8.4(8)	7.0(7)	8.9(8)	0.1(6)	1.5(6)	-0.0(6)
C(13)	0.318(2)	0.298(1)	0.1805(7)	12(1)	8(1)	7.8(8)	0.6(7)	3.8(7)	-0.8(6)
C(14)	0.405(2)	0.407(2)	0.1802(7)	8.0(8)	12(1)	7.9(8)	0.8(8)	2.8(6)	0.3(8)
C(15)	0.446(1)	0.483(1)	0.2413(7)	5.6(5)	8.2(9)	12(1)	0.3(5)	1.8(6)	1.9(8)
C(16)	0.394(1)	0.454(1)	0.2994(6)	5.8(6)	7.6(8)	8.6(7)	0.2(5)	2.0(5)	-0.9(6)
B	-0.348(2)	0.225(1)	0.0503(7)	6.4(7)	6.4(7)	7.0(7)	1.8(6)	0.0(6)	-0.5(6)
F(1)	-0.486(1)	0.163(1)	0.0555(5)	10.6(6)	18.0(9)	12.2(7)	-3.5(6)	-0.4(5)	4.6(7)
F(2)	-0.250(3)	0.152(2)	0.043(2)	36(3)	19(2)	62(4)	15(2)	36(3)	17(2)
F(3)	-0.290(4)	0.264(3)	0.106(1)	44(4)	66(5)	20(2)	-39(4)	14(2)	-17(2)
F(4)	-0.375(2)	0.310(2)	0.004(1)	18(1)	26(2)	34(2)	1(1)	4(1)	19(2)

[a] Estimated standard deviations in the least signicant figure(s) are given in parentheses in this and all subsequent tables.

[b] The form of the thermal ellipsoid is: exp[-2*PI²(a*²U11h²+b*²U22k²+c*²U33l²+2a*b*U12hk+2a*c*U13hl+2b*c*U23kl)]. The quantities given in the table are the thermal coefficients x 10².

Table 5. Idealized Positional and Thermal Parameters For the Hydrogen Atoms of [Cp2W(NH2NPh)][BF4].

Atom	x	y	z	B(A')	Atom	x	y	z	B(A')
NH(1)[a]	0.25(1)	0.49(1)	0.404(5)	7(3)	H(3)	-0.0746	0.0157	0.3358	6.54
NH(2)[a]	0.37(2)	0.37(1)	0.452(6)	8(3)	H(4)	0.2330	0.0355	0.3847	8.30
H(12)	0.2022	0.1906	0.2370	7.33	H(5)	0.2983	0.1585	0.5016	7.33
H(13)	0.2924	0.2426	0.1385	8.71	H(6)	-0.2415	0.3825	0.4179	8.71
H(14)	0.4465	0.4277	0.1407	8.19	H(7)	-0.0317	0.5436	0.4052	8.19
H(15)	0.5104	0.5608	0.2414	7.94	H(8)	0.0380	0.4937	0.2908	7.94
H(16)	0.4202	0.5089	0.3399	7.28	H(9)	-0.1286	0.3018	0.2328	7.28
H(1)	0.0310	0.2147	0.5250	7.28	H(10)	-0.3014	0.2331	0.3113	7.28
H(2)	-0.1995	0.1265	0.4225	7.28					

[a] Refined as an isotropic atom.

Table 6. Selected Interatomic Distances (Å) in $[(\eta^5\text{-}C_5H_5)_2W(NH_2NPh)][BF_4]$.

BONDED CONTACTS

W-N(1)	2.156(9)	C(3)-C(4)	1.38(2)
W-N(2)	2.034(9)	C(4)-C(5)	1.43(2)
W-C(1)	2.28(1)	C(5)-C(1)	1.41(2)
W-C(2)	2.29(1)	C(6)-C(7)	1.34(2)
W-C(3)	2.33(2)	C(7)-C(8)	1.36(2)
W-C(4)	2.36(1)	C(8)-C(9)	1.32(2)
W-C(5)	2.33(1)	C(9)-C(10)	1.49(3)
W-C(6)	2.29(1)	C(10)-C(6)	1.35(3)
W-C(7)	2.34(1)	C(11)-C(12)	1.38(2)
W-C(8)	2.26(1)	C(12)-C(13)	1.37(2)
W-C(9)	2.28(1)	C(13)-C(14)	1.37(2)
W-C(10)	2.29(1)	C(14)-C(15)	1.39(2)
N(1)-N(2)	1.43(1)	C(15)-C(16)	1.37(2)
N(1)-NH(1)	1.08(11)	C(16)-C(11)	1.39(1)
N(1)-NH(2)	0.97(13)	B-F(1)	1.38(2)
N(2)-C(11)	1.39(1)	B-F(2)	1.18(2)
C(1)-C(2)	1.41(2)	B-F(3)	1.14(2)
C(2)-C(3)	1.40(2)	B-F(4)	1.24(2)

NON-BONDED CONTACTS

F(1)-NH(2)	2.1(1)[a]	H(2)-C(6)	2.90
F(2)-NH(1)	2.0(1)[b]	H(8)-C(11)	2.72
F(3)-H(9)	2.48	H(10)-C(2)	2.78
NH(1)-H(16)	2.19	H(12)-N(2)	2.52
NH(1)-H(8)	2.43	H(16)-N(1)	2.60
H(2)-H(10)	2.37	H(16)-N(2)	2.67
H(2)-C(10)	2.68		

HINDERED ROTOR PARAMETERS

Cp(1)		Cp(2)	
C-C	1.421(6)	C-C	1.423(6)
Bd = 1.82[c]		Bd = 0.42	

[a] NH(2) is associated with the molecule at the general equivalent position x, ½-y, ½+z.

[b] NH(1) is associated with the molecule at the general equivalent position x, ½+y, ½-z.

[c] Bd is the barrier to libration in units of 2kT, where k is the Boltzmann constant and T is the temperature.

Table 7. Selected Angles (deg) in $[(\eta^5\text{-}C_5H_5)_2W(H_2NNPh)][BF_4]$

Bond Angles

N(1)-W-N(2)	39.7(3)	C(1)-C(2)-C(3)	109(1)
W-N(1)-NH(1)	115 (6)	C(2)-C(3)-C(4)	108(1)
W-N(1)-NH(2)	133 (8)	C(3)-C(4)-C(5)	108(1)
W-N(1)-N(2)	65.6(5)	C(4)-C(5)-C(1)	108(1)
W-N(2)-N(1)	74.8(6)	C(5)-C(1)-C(2)	106(1)
W-N(2)-C(11)	140.1(6)	C(6)-C(7)-C(8)	108(2)
N(2)-N(1)-NH(1)	117 (5)	C(7)-C(8)-C(9)	112(2)
N(2)-N(1)-NH(2)	112 (7)	C(8)-C(9)-C(10)	105(2)
NH(1)-N(1)-NH(2)	107 (10)	C(9)-C(10)-C(6)	105(2)
N(1)-N(2)-C(11)	119.4(9)	C(10)-C(6)-C(7)	111(2)
N(2)-C(11)-C(12)	117 (1)	F(1)-B-F(2)	111(2)
N(2)-C(11)-C(16)	124.2(9)	F(1)-B-F(3)	104(2)
C(11)-C(12)-C(13)	121 (1)	F(1)-B-F(4)	114(1)
C(12)-C(13)-C(14)	120 (1)	F(2)-B-F(3)	103(2)
C(13)-C(14)-C(15)	118 (1)	F(2)-B-F(4)	112(2)
C(14)-C(15)-C(16)	121 (1)	F(3)-B-F(4)	112(2)
C(15)-C(16)-C(11)	119 (1)	N(1)-NH(1)-F(2)	139(8)[a]
C(16)-C(11)-C(12)	119 (1)	N(1)-NH(2)-F(1)	154(10)[b]
CR1-W-CR2	136.8		

Torsion Angles

NH(1)-N(1)-N(2)-C(11)	32.3	C(3)-CR1-CR2-C(9)	33.5
C(1)-CR1-CR2-C(6)	31.2	C(4)-CR1-CR2-C(8)	34.7
C(2)-CR1-CR2-C(10)	32.1	C(5)-CR1-CR2-C(7)	33.2

Vector-Plane Normal Angles

N(2)-N(1)	NH(1)-N(1)-NH(2)	44 (7)[c]
N(2)-C(11)	W-N(1)-N(2)	55.5(8)[c]

[a] F(2) is associated with the molecule at the general equivalent position $\bar{x}$, ½+y, ½-z.

[b] F(1) is associated with the molecule at the general equivalent position x, ½-y, ½+z.

[c] Angle between the vector defined by the first two atoms and the normal to the plane defined by the last three atoms.

Table 8. Least-Squares Plane Calculations[a]

plane no.	equation
1	-0.2728X + 0.7327Y - 0.6235Z + 1.8482 = 0
2	0.1126X + 0.8539Y - 0.5081Z + 3.3639 = 0
3	-0.6073X + 0.6045Y - 0.5155Z - 1.1396 = 0
4	0.1702X - 0.4923Y - 0.8536Z + 7.8509 = 0
5	-0.7532X + 0.5300Y - 0.3897Z + 0.9023 = 0
6	-0.8250X + 0.3563Y - 0.4387Z + 1.8727 = 0

Deviations from the Planes (Å)

	Plane no.					
Atom	1	2	3	4	5	6
W	0.0	1.9839(5)[b]	-1.9695(5)[b]	0.0		
N(1)	0.0			-0.774(9)[b]		0.0
N(2)	0.0			0.639(8)[b]		0.0
C(1)		0.01(1)				
C(2)		-0.01(1)				
C(3)		0.01(2)				
C(4)		0.00(2)				
C(5)		0.01(2)				
C(6)			-0.02(2)			
C(7)			0.02(2)			
C(8)			-0.01(2)			
C(9)			0.01(2)			
C(10)			0.00(2)			
C(11)	0.79(1)[b]				-0.01(1)	0.0
C(12)					0.03(1)	
C(13)					-0.03(2)	
C(14)					0.02(1)	
C(15)					-0.01(1)	
C(16)					0.00(1)	
CR1				0.0		
CR2				0.0		

Dihedral Angles Between Planes

Plane A	Plane B	angle (deg)
1	2	24.3
1	3	21.6
1	4	82.8
1	5	33.2
1	6	40.6
2	3	44.8
5	6	11.9

[a]X, Y and Z are the orthogonal coordinates (Å) with X along the a axis, Y in the (a-b) plane and Z along the c^* axis.

[b]Not included in the least squares plane calculation.

DESCRIPTION OF STRUCTURE

The structure of $[(\eta^5\text{-}C_5H_5)_2W(NH_2NPh)][BF_4]$ consists of four monomeric anions and cations per unit cell, as shown in Figure 3. The description of the tetrafluoroborate anion is somewhat inadequate owing to the disorder of this group. As a result, the thermal parameters for the four fluorine atoms are large (Table 4) and much of the unassigned electron density in the final difference Fourier map lies in the region around the anion. In spite of the disorder, however, the anion clearly shows the expected tetrahedral configuration about the boron atom. The B-F distances, which range from 1.14(2) to 1.38(2) Å (Table 6) are somewhat shorter than other reported values,[21] but are not unreasonable considering the disorder. In addition the F-B-F angles, ranging from 103(2)° to 114(1)° (Table 7) are as expected. There are two significant non-bonded contacts between the fluorine atoms and the hydrogen atoms of the hydrazido ligand (F(1)-NH(2), 2.1(1)Å; F(2)-NH(1), 2.0(1) Å), both of which are much less than the sum of their van der Waals radii (2.57 Å).[22] The corresponding N(1)-NH(1)-F(2) and N(1)-NH(2)-F(1) angles are 139(8)° and 154(10)°, respectively.

The $[(\eta^5\text{-}C_5H_5)_2W(NH_2NPh)]^+$ cation can be viewed as having pseudotetrahedral coordination about the tungsten atom, with the $(\eta^5\text{-}C_5H_5)$ rings each occupying one coordination site and the two nitrogen atoms of the "side-on"

bonded phenylhydrazido(1-) ligand occupying the other sites. However, the coordination angles are significantly distorted from the ideal geometry owing to the large bulk of the Cp rings and the small bite angle of the hydrazido ligand; the CR1-W-CR2 angle is 136.8° while the N(1)-W-N(2) angle is 39.7(3)°. There are no unusually short non-bonded interactions between the two cyclopentadienyl rings. The metal-carbon bond lengths are in the range 2.28(1) to 2.36(1) Å for Ring 1 (average, 2.32(3) Å) and 2.26(1) to 2.34(1) for Ring 2 (average, 2.29(3) Å). These M-C distances are quite typical for $CpML_n$ compounds,[23,24] and agree well with the values found for the monoinserted product, $[Cp_2WH(NNHC_6H_4F)][PF_6]$.[7] The perpendicular distances between the metal and the ring planes are 1.9839(5) Å (Ring 1) and 1.9695(5) Å (Ring 2). They agree well with the metal-ring center distances (Ring 1, 1.985 Å and Ring 2, 1.971) indicating that each ring is well centered above the metal atom.

A comparison of Cp-M-Cp angles within a series of Cp_2ML_2 complexes containing staggered Cp groups indicates that the CR1-W-CR2 angle (136.8°) in the present compound, although comparable to other values (126.0 to 135.3°), is somewhat larger. An analysis of these angles[23] indicates that the larger angles tend to correspond to shorter Cp-M distances, implying that these angles are governed primarily by intramolecular repulsions. The small N(1)-W-N(2) angle (39.7(3)°) in the present compound probably results in a less crowded

environment for the Cp rings and consequently in a larger CR1-W-CR2 angle. In $[Cp_2Ti(\eta^2\text{-}C_6H_5CN\text{-}2,6\text{-}(CH_3)_2C_6H_3)]$,[25] which also has a small ligand bite angle (35.1(2)°), the Cp-Ti-Cp angle is again larger than that expected from the Cp-Ti distances.

The cyclopentadienyl rings assume a staggered conformation with C-CR1-CR2-C torsion angles averaging 32.9° (see Table 7). Other studies on similar systems have indicated that these ring conformations are governed primarily by crystal packing.[23] The carbon atoms in each of the rings are coplanar to within 0.01 Å (Ring 1) and 0.02 Å (Ring 2). Within each ring the C-C bond distances are in the range 1.38(2) to 1.43(2) Å for Ring 1, (average, 1.41(3) Å) and 1.32(2) to 1.49(2) Å for Ring 2, (average, 1.37(6) Å). These average values are shorter than the predicted value of 1.43 Å.[26] However, this apparent shortening is a consequence of thermal libration of the rings and is a general feature of $\eta^5\text{-}C_5H_5$ compounds where the Cp rings are refined as individual atoms. In this respect the hindered rotor refinement is useful since the ring radii are allowed to vary as the ring librates about the metal-CR axis. This model for the Cp groups minimizes the ring contraction that is so common whan individual atom refinements are used.[23] From the hindered rotor refinement the C-C distances (1.421(6) and 1.423 (6) Å for rings 1 and 2, respectively) agree very well with each other and with the predicted value. In the individual atom refinement of the Cp rings the group with the shorter

average C-C distance (Ring 2) also has the higher thermal parameters and corresponds to the group having the lower barrier to libration in the hindered rotor description (Table 6).

The phenylhydrazido ligand is side-on bonded to the W atom through the two nitrogen atoms. The W-N(1)-N(2) plane essentially bisects the CR1-W-CR2 angle and the dihedral angle between these planes is 82.8° (Table 8). The two metal-nitrogen bonds are noticeably different, with W-N(1), involving the four-coordinate nitrogen atom (2.156(9) Å), being significantly longer than W-N(2) (2.034(9) Å), which involves the three-coordinate nitrogen atom. The shorter distance may result from donation of the available lone pair on N(2) to the metal, although the W atom formally has an 18-electron configuration already. Similar electron donation from the chloro ligands to the metal atoms is believed responsible for the short M-Cl bonds in Cp_2MCl_2 complexes.[23] The possible involvement of the free lone pair on N(2) may also explain the phenyl group orientation (see Figure 5) and the solution NMR characteristics[5,6] (*vide infra*). The W-N bonds can be compared to typical W-N single bonds in pyridine complexes which lie in the range 2.23 to 2.32 Å.[27,28] On the other hand, hydrazido (2-) complexes, with M-N bond orders greater than one, typically have M-N bond lengths of *ca.* 1.75 Å.[29] While there are no other reported dihapto

hydrazido(1-) metal compounds, a comparison can be made with the following related compounds: $\{(\eta^5\text{-}C_5H_5)Mo(NO)I\}_2$-$(\mu N\text{-}NMe_2)$[30] and $[(\eta^5\text{-}C_5H_5)Mo(NO)I(NH_2NHPh)][BF_4]$.[31] In these species the Mo-N bonds involving the four-coordinate nitrogen atoms (2.133(12) to 2.184(3) Å) are again significantly longer than that of the three-coordinate nitrogen atom (2.058(12) Å), and both classes of W-N bonds compare well with the analogous distances in the present hydrazido(1-) complex. As a consequence of the above asymmetric bonding of the hydrazido(1-) ligand, the two nitrogen atoms are not equally spaced from the CR1-W-CR2 plane; instead N(1) is 0.774(9) Å from the plane, and N(2) is displaced 0.639(8) Å from this plane.

The N-N bond length in the title complex (1.43(1) Å) compares well with the values for the two molybdenum hydrazido compounds (1.400(17) Å [30] and 1.430(5)) [31] and is typical of an N-N single bond. By comparison, a characteristic N-N double bond is *ca.* 1.23 Å.[32] Both hydrogen atoms on N(1) were located and refined, resulting in normal N-H bond distances of 1.08(11) Å for N(1)-NH(1) and 0.97(13) Å for N(1)-NH(2). The NH(1)-N(1)-NH(2) angle is 107(10)° close to that expected for a tetrahedral coordination about the nitrogen, and the angle of the N(2)-N(1) vector to the normal of the NH(1)-N(1)-NH(2) plane is 44(7)°, comparable to the calculated value of *ca.* 35.3° for an idealized tetrahedral coordination. No electron density that would be consistent

with a hydrogen atom is observed in the vicinity of N(2). This is consistent with the solution NMR studies[6] which show both protons on N(1) and none on N(2). It is somewhat surprising that both hydrazido hydrogen atoms are bonded to N(1) since in the initial monoinserted product the hydrogen atom and the phenyl ring are bonded to the same nitrogen atom,[6,7] indicating that in the second insertion process the transfer of a hydrogen atom from W to N(1) is accompanied by a hydrogen transfer from N(2) to N(1). The N(2)-C(11) bond (1.39(1) Å) is somewhat shorter than a normal N-C single bond (1.43 Å) involving an sp^2 hybridized carbon atom,[22] but is not particularly unusual. The C-C lengths in the phenyl ring are all reasonable and the carbon atoms of the ring are coplanar to within 0.03 Å (Table 8). The phenyl ring is bent out of the W-N(1)-N(2) plane by 34.5(8)° towards Cp ring 2 with C(11) being 0.79(1) Å out of this plane (see Figure 5).

Although the phenyl group orientation on N(2) is characteristic of sp^3 hybridization of this atom, some distortion is evident. Instead of an eclipsed configuration about the N(1)-N(2) bond, the phenyl group is staggered with respect to the N(1) hydrogen atoms (the NH(1)-N(1)-N(2)-C(11) torsion angle is 32.3°). This twist about the N(1)-N(2) bond may result because of involvement of the lone pair of electrons on N(2) in bonding with the metal atom, as the twist is in the proper direction for such an interaction

and the short W-N(2) bond is consistent with some multiple bond character (*vide supra*). It is also possible that this distortion from eclipsed conformations about N(1) and N(2) may be steric in origin, resulting from non-bonded interactions between the cyclopentadienyl ring 2 and the phenyl ring pushing the phenyl ring towards the W-N(1)-N(2) plane. The only such contact which is significant (C(11)-H(8) = 2.72 Å) would favour this distortion. However, we have already noted that the CR1-W-CR2 angle is greater than is generally observed, indicating that the cyclopentadienyl groups are not overly crowded. The staggered conformation may also result from steric interactions between NH(1) and H(16) since this contact (2.19 Å) is rather short.

DISCUSSION

There is a notable lack of structural information on Cp_2ML complexes, in which L is a side-on coordinated ligand, thereby limiting any comparison of structural parameters. Only the present structure and that of $[Cp_2Ti(\eta^2\text{-}C_6H_5CN\text{-}2,6\text{-}(CH_3)_2C_6H_3)]$[25] are known to us. At the first glance the structural differences between these complexes and the related Cp_2ML_2 species seem to result primarily from the reduced steric demands of the η^2-coordinated ligands as compared to the two sigma bonded ligands (*vide supra*). However, a more detailed analysis of the differences in the two types of systems must await further structural character-

izations of Cp_2ML complexes containing side-on coordinated ligands.

The structural determination of the present complex, besides providing some of this badly needed information has also proven useful in understanding the ^1H NMR data[6] which indicate that the two cyclopentadienyl rings are equivalent, even at low temperature. This equivalence could result from the complete planarity of the hydrazido(1-) ligand framework in the plane bisecting the angle between the two Cp rings, or from a fluctional process which averages the Cp ring environments. The solid state data indicate that the two cyclopentadienyl rings are inequivalent since the phenyl group is significantly displaced from the W-N(1)-N(2) plane towards Cp Ring 2. As suggested earlier, this phenyl ring orientation may result from involvement of the free lone pair on atom N(2) in bonding with the W atom. This proposed bonding would account for the short W-N(2) bond length and, if the Cp equivalence results from "flipping" of the phenyl ring from one side of the W-N(1)-N(2) plane to the other, could also explain the facility of this process. The involvement of the N(2) lone pair in bonding with the W atom would allow the "flipping" mechanism to proceed by a concerted process with the simultaneous involvement of two N(2) electron pairs with the W atom.

The $[(\eta^5\text{-}C_5H_5)_2W(NH_2NPh)]^+$ cation is believed to be the first structurally characterized complex containing a hydra-

zido(1-) ligand,[33] an important intermediate species in model systems for the reduction of dinitrogen. Although Hidai and coworkers[34] have reported the structure of a species which they claim is a hydrazido(1-) complex, $[WClBr_2(N_2H_3)(PMe_2Ph)_3]$, their crystallographic evidence does not support this claim, and even the authors admit doubt concerning its formulation. Certainly in solution their evidence for a species containing the $NHNH_2$ ligand is convincing, but their solid state structure is more characteristic of a hydrazido(2-) ligand with a $W{=}N{=}NH_2$ moiety. All of their structural parameters, including the short W-N bond (1.80(4) Å), the almost linear W-N-N fragment (177(5)°) and the N-N distance (1.24(6) Å) which is characteristic of an N=N double bond, support a terminally bonded hydrazido(2-) formulation. Furthermore, this structure bears a remarkable resemblance to the hydrazido(2-) complex, $[W(\text{quinolin-8-olate})(NNH_2)(PMe_2Ph)_3]I$, recently reported by Chatt and coworkers.[29] The authors' suggestion[34] that the complex $[WClBr_2(N_2H_3)(PMe_2Ph)_3]$ may actually contain a $W{-}N{-}NH_3^+$ moiety is also not consistent with the observed structural parameters, in particular the short N-N distance. Our formulation of the title complex as a hydrazido(1-) species, on the other hand, is quite unambiguous with all parameters being consistent with this formulation; even the hydrazido hydrogen atom positions are well defined.

The present structural determination is particularly relevant to our understanding of dinitrogen reduction. In-

sertion reactions of aryldiazo cations into metal-hydride bonds have long been considered as useful model systems for nitrogen fixation. The reaction of Cp_2WH_2 with $(N_2Ar)^+$ produces not only the mono-inserted hydrazido(2-) product, $[Cp_2WH(NNHAr)]^+$, [7] but also the doubly-inserted hydrazido(1-) product, $[Cp_2W(NH_2NAr)]^+$. The mechanism of the rearrangement from the mono-inserted complex, a monohydrido species with a doubly bent hydrazido ligand[7] to that of the double insertion product, where both hydrogens are coordinated to the first nitrogen atom, and the ligand is side-on coordinated, is unknown, but of considerable interest. In addition, the latter species has the diazo moiety activated by the W atom, suggesting the possibility of further reduction of this ligand.

Double insertion reactions involving Cp_2MH_2 compounds (M = Mo,W) have been reported,[35] for example in the reactions of azobenzene and diazofluorene. However the double insertion products were not isolated, undergoing instead, loss of the reduced molecule and subsequent attack of the "Cp_2M" species by excess ligand. As such, the title complex represents the first characterized species resulting from the double insertion into both metal-hydride bonds of a dihydride complex. This compound is one step closer to a totally reduced N_2Ph^+ cation than the products obtained from the usual monoinsertion reactions and represents an important intermediate in model system studies for the reduction of dinitrogen.

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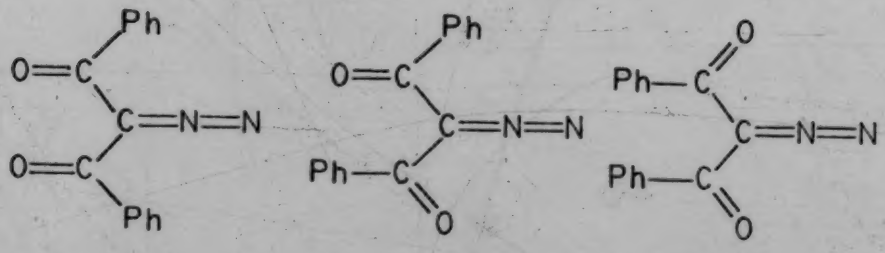
Chapter III.

The Structure of Dibenzoyldiazomethane.

INTRODUCTION

Diazoalkane molecules have been studied for many years and their chemistry is well documented.[1] Although synthetically, they are extremely useful reagents,[2] very few structural studies have been done on free diazoalkane molecules, owing to the limited stability of most diazo groups. Dibenzoyldiazomethane, ($C_6H_5COCN_2COC_6H_5$), is unusual in this regard, in that the molecule may be isolated as a relatively stable, crystalline product.

In dibenzoyldiazomethane, a planar conformation will be favored owing to the possibility of π-delocalization over the molecular framework.[3] For such a planar molecule, three geometries are possible, having the carbonyl and diazo functions either cis or trans relative to each other, about the C-C single bonds.



s-trans-s-trans s-trans-s-cis s-cis-s-cis

Based on e.s.r. studies of the carbene radical obtained through photolysis of the parent dibenzoyldiazomethane molecule, Murai, Torres and Strausz[4] concluded that the s-trans-s-cis conformation was favored. In contrast, a study based on ^{1}H NMR and dipole measurements[5] predicted the s-cis-s-cis conformation for a series of related, alkyl substituted analogues, $RCOCN_2COR'$ ($R,R' = CH_3, C_2H_5, CH(CH_3)_2, C(CH_3)_3$). The structural determination of the title species was therefore necessary in order to unambiguously establish the molecular conformation.

In addition, the chemistry of diazoalkanes with metal complexes have been of interest in recent years owing to the tremendous diversity of this chemistry[6] (see Chapter I). Diazoalkanes can react as 1,3 dipoles or as nucleophiles through either the carbon or the terminal nitrogen atom, producing a variety of metal species, some containing the intact diazoalkane molecule, while others have only fragments of the parent species (see Chapter I). Since part of these studies involved the chemistry of dibenzoyldiazomethane with transition metal complexes (see Chapter V), the structural determination of this diazoalkane molecule was of importance in order to form a basis for structural comparisons with the coordinated species and to assist in understanding the metal chemistry of this species. The X-ray structural determination of dibenzoyldiazomethane was therefore undertaken for the above reasons.

EXPERIMENTAL

Yellow crystals of dibenzoyldiazomethane, prepared by the reaction of $(C_6H_5CO)_2CH_2$ with *p*-toluene sulfonylazide[7] and recrystallized twice from ethanol were kindly supplied by Dr. M. Torres and Professor O.P. Strausz (University of Alberta). A suitable crystal was mounted in air on a glass fibre, and precautions were taken to minimize the exposure of the crystal to light, throughout the data collection.

Preliminary Weissenberg and precession photographs indicated the monoclinic space group $P2_1/c$ with systematic absences $h0\ell$, $\ell = 2n+1$ and $0k0$, $k = 2n+1$. However, owing to an unfavorable β angle (*ca.* 123°) the non-standard $P2_1/n$ setting with a somewhat more favorable β angle (118.18°) was chosen. The cell parameters are listed in Table 9 along with the pertinent crystal data and intensity collection details. Otherwise the data collection proceeded as outlined in Chapter II.

STRUCTURE SOLUTION AND REFINEMENT

The structure was solved by direct methods, using the program MULTAN.[8] The solution was based on 231 reflections having $|E| > 1.40$ and 1617 phase relationships. The E-map corresponding to the solution with the best figures of merit revealed the positions of the 15 carbon atom backbone. All other non-hydrogen atoms were located in a subsequent E-map obtained by recycling MULTAN.[9] All hydrogen atoms were located in subse-

Table 9. Summary of Data and Intensity Collection for Dibenzoyldiazomethane.

Compound	$(C_6H_5)COCN_2CO(C_6H_5)$
Formula	$C_{15}H_{10}N_2O_2$
Formula Weight	250.26
Cell Parameters	
a	9.5631(9) Å
b	14.5638(19) Å
c	10.1538(11) Å
β	118.184(9)°
V	1246.6 Å^3
Z	4
Density	1.333 g·cm^{-3} (calcd.)
Space Group	C_{2h}^5 - $P2_1/n$
Crystal Dimensions	0.432 x 0.357 x 0.084 mm
Crystal Volume	0.0130 mm^3
Crystal Shape	monoclinic prism with major faces of the form (010), (0$\bar{1}\bar{2}$), (01$\bar{1}$)
Temperature	20°C
Radiation	Cu Kα (λ = 1.540562 Å)
μ	7.015 cm^{-1}
Takeoff Angle	2.75°
Scan Speed	2° in 2θ/min
Scan Range	0.90° below $K\alpha_1$ to 0.90° above $K\alpha_2$
Background Counting Time	10 s (2θ ≤ 77.5°); 20 s (77.5° < 2θ ≤ 122.5°)
2θ Limits	3.0° - 122.5°

Table 9, Continued

2θ Limits for Centered Reflections	$50.0° \leq 2\theta \leq 70.0°$
Final Number of Parameters	172
Unique Data Collected	2010
Unique Data Used ($F_o^2 \geq 3\sigma(F_o^2)$)	1471
Error in Observation of Unit Weight	1.40 electrons
R	0.038
R_w	0.057

quent electron density difference maps. Full matrix least-squares refinement techniques were used, with atomic scattering factors from Cromer and Waber[10] used for all atoms except hydrogen, for which the values from Stewart, Davidson and Simpson[11] were used. All non-hydrogen atoms were refined as individual atoms having anisotropic thermal parameters. The hydrogen atoms were included as fixed contributions in their idealized positions, with thermal parameters of 1 $\AA^2$ greater than the equivalent isotropic B for the corresponding carbon atom. Absorption corrections were not applied owing to the very small linear absorption coefficient (7.015 cm^{-1}). In the final electron density difference map, the top twenty residuals were less than 0.10 $e/\AA^3$ and were distributed randomly throughout space. In earlier difference maps, a typical H atom had a value of 0.47 $e/\AA^3$. A more detailed discussion of the methods used in the structure solution and refinement is outlined in Chapter II.

RESULTS

A stereoview of the unit cell is presented in Figure 6. The crystallographic *a* axis is going into the page, the *b* axis runs from the bottom to the top, and the *c* axis goes from left to right across the diagram. Figure 7 (50% ellipsoids) shows the numbering scheme used in the molecule (hydrogens have the same number as their attached carbon atoms). The final positional and thermal parameters for the non-hydrogen atoms are in Table 10 and the idealized

positional and thermal parameters for the hydrogen atoms are given in Table 11. Relevant interatomic distances (bonded and non-bonded) are listed in Table 12, while bond angles and torsion angles are in Table 13. A listing of the observed and calculated structure amplitudes is available.[12]

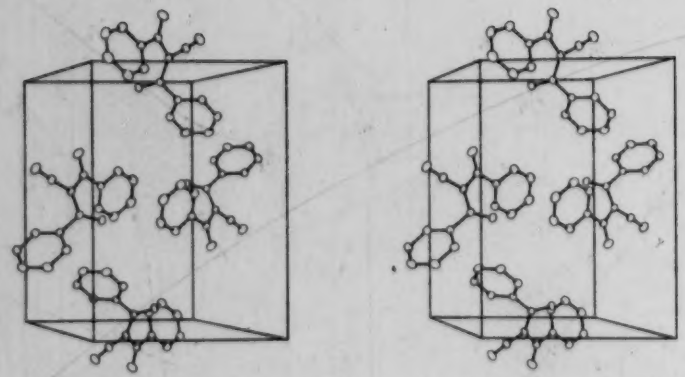


Figure 6. Cell Packing Diagram of $PhCOCN_2COPh$.

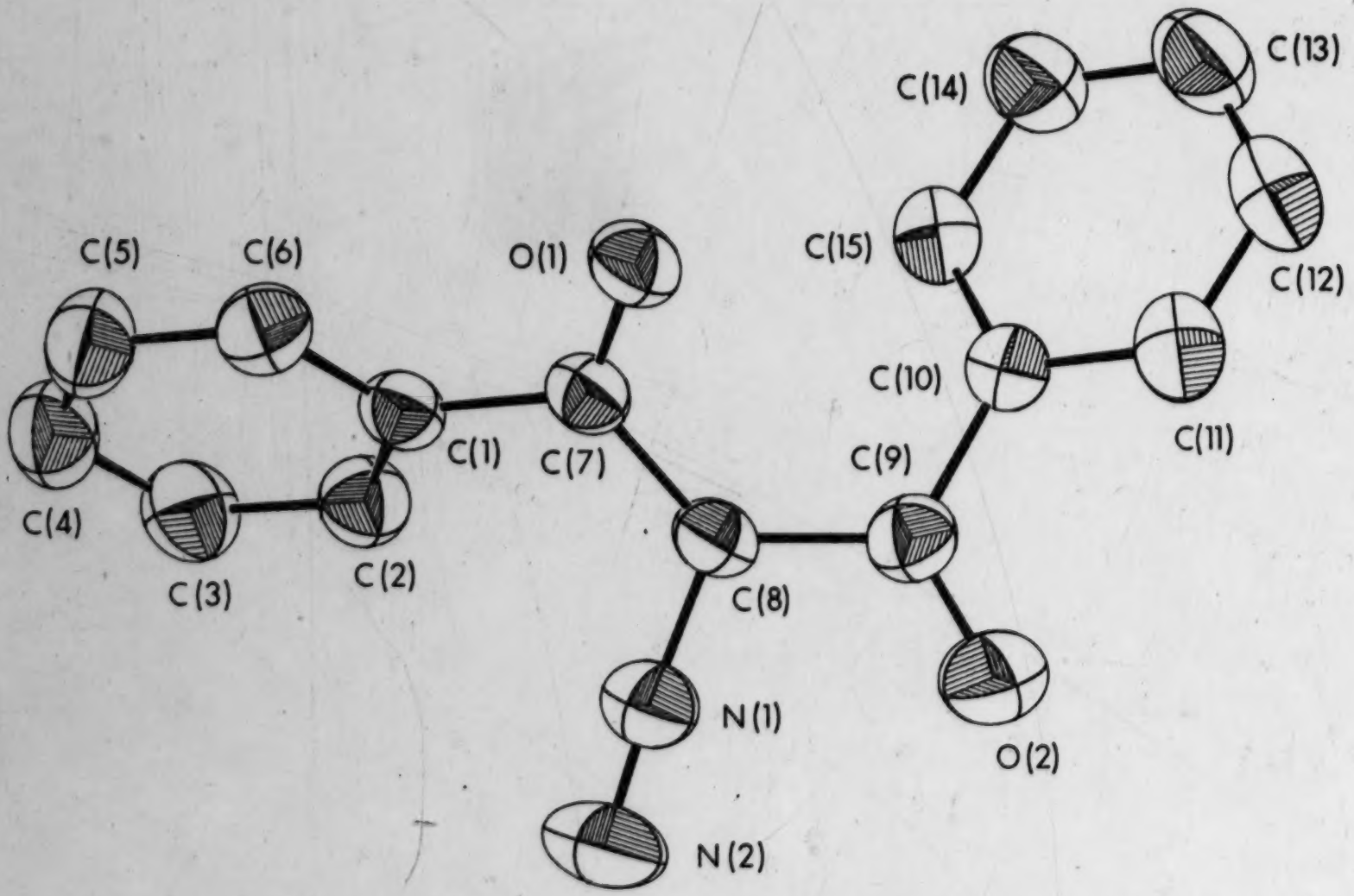


Figure 7. Perspective View of Dibenzoyldiazomethane.

Table 10. Positional and Thermal Parameters for the Non-Hydrogen Atoms of [PhCOCN2COPh].

Atom	x[a]	y	z	U11[b]	U22	U33	U12	U13	U23
O(1)	0.6692(2)	1.06999(10)	0.6156(1)	5.85(9)	6.45(9)	3.77(7)	0.49(7)	2.10(6)	-0.42(6)
O(2)	0.8448(2)	0.8184(1)	0.5629(2)	8.4(1)	4.87(8)	7.0(1)	1.18(8)	2.55(8)	-0.93(7)
N(1)	0.6458(2)	0.9197(1)	0.3456(2)	6.4(1)	5.6(1)	4.48(9)	-0.21(9)	2.26(8)	-0.51(9)
N(2)	0.5815(3)	0.8797(2)	0.2404(2)	10.1(2)	8.2(1)	5.3(1)	-1.3(1)	2.4(1)	-2.4(1)
C(1)	0.5869(2)	1.1121(1)	0.3644(2)	3.9(1)	4.4(1)	3.94(9)	-0.60(8)	1.40(8)	-0.23(8)
C(2)	0.6369(2)	1.1148(1)	0.2557(2)	5.1(1)	5.7(1)	4.8(1)	0.13(9)	2.43(9)	-0.01(9)
C(3)	0.5662(3)	1.1753(2)	0.1366(2)	7.5(1)	6.1(1)	4.6(1)	-0.1(1)	2.9(1)	0.5(1)
C(4)	0.4449(3)	1.2313(2)	0.1235(2)	7.6(2)	5.0(1)	5.3(1)	0.0(1)	1.9(1)	0.8(1)
C(5)	0.3953(3)	1.2296(2)	0.2308(3)	6.0(1)	5.0(1)	7.2(1)	1.0(1)	2.4(1)	0.5(1)
C(6)	0.4674(2)	1.1714(1)	0.3522(2)	5.2(1)	4.8(1)	5.6(1)	0.16(9)	2.69(10)	-0.07(9)
C(7)	0.6616(2)	1.0496(1)	0.4954(2)	3.6(1)	4.9(1)	3.81(9)	-0.37(8)	1.38(8)	-0.24(8)
C(8)	0.7266(2)	0.9618(1)	0.4776(2)	4.8(1)	5.0(1)	3.41(9)	-0.19(9)	1.45(8)	-0.55(8)
C(9)	0.8454(2)	0.9001(1)	0.5903(2)	5.2(1)	4.9(1)	4.9(1)	0.56(9)	2.57(9)	-0.04(9)
C(10)	0.9681(2)	0.9398(1)	0.7333(2)	4.5(1)	5.2(1)	4.4(1)	0.80(9)	2.05(9)	-0.01(8)
C(11)	1.0351(3)	0.8834(2)	0.8583(2)	5.8(1)	6.5(1)	5.6(1)	1.0(1)	2.4(1)	1.0(1)
C(12)	1.1530(3)	0.9166(2)	0.9923(2)	6.3(1)	10.0(2)	4.6(1)	1.5(1)	1.7(1)	1.2(1)
C(13)	1.2058(3)	1.0050(2)	1.0018(3)	5.1(1)	9.7(2)	5.5(1)	0.8(1)	0.9(1)	-1.3(1)
C(14)	1.1429(3)	1.0610(2)	0.8779(3)	4.8(1)	7.0(1)	6.7(1)	-0.0(1)	1.5(1)	-1.3(1)
C(15)	1.0231(2)	1.0289(1)	0.7440(2)	4.6(1)	5.6(1)	5.3(1)	0.6(1)	1.73(9)	0.24(10)

[a] Estimated standard deviations in the least signicant figure(s) are given in parentheses in this and all subsequent tables.

[b] The form of the thermal ellipsoid is: exp[-2*PI'(a*'U11h'+b*'U22k'+c*'U33l'+2a*b*U12hk+2a*c*U13hl+2b*c*U23kl)]. The quantities given in the table are the thermal coefficients x 10'.

Table 11. Idealized Positional and Thermal Parameters for the Hydrogen Atoms of [PhCOCN2COPh].

Atom	x	y	z	B(A²)	Atom	x	y	z	B(A²)
H(2)	0.7191	1.0749	0.2632	5.04	H(11)	0.9999	0.8216	0.8515	5.81
H(3)	0.6017	1.1775	0.0636	5.81	H(12)	1.1884	0.8783	1.0781	6.81
H(4)	0.3953	1.2718	0.0405	6.09	H(13)	1.2857	1.0281	1.0944	6.86
H(5)	0.3114	1.2690	0.2217	6.00	H(14)	1.1819	1.1217	0.8844	6.23
H(6)	0.4351	1.1715	0.4276	5.09	H(15)	0.9785	1.0677	0.6589	5.25

Table 12. Selected Interatomic Distances (Å) for $(PhCO)_2CN_2$.

BONDED CONTACTS

N(1) - N(2)	1.112(2)	C(1) - C(2)	1.395(3)
N(1) - N(2)*	1.151(3)	C(2) - C(3)	1.387(3)
N(1) - C(8)	1.339(2)	C(3) - C(4)	1.372(3)
C(7) - O(1)	1.224(2)	C(4) - C(5)	1.379(3)
C(7) - O(1)*	1.240(2)	C(5) - C(6)	1.382(3)
C(9) - O(2)	1.221(2)	C(6) - C(1)	1.390(3)
C(9) - O(2)*	1.250(2)	C(10) - C(11)	1.389(3)
C(1) - C(7)	1.488(2)	C(11) - C(12)	1.381(3)
C(7) - C(8)	1.469(3)	C(12) - C(13)	1.370(4)
C(8) - C(9)	1.477(3)	C(13) - C(14)	1.377(3)
C(9) - C(10)	1.487(3)	C(14) - C(15)	1.382(3)
		C(15) - C(10)	1.384(3)

NON-BONDED CONTACTS

O(1) - C(6)	2.861(2)	C(7) - H(15)	2.694(2)
O(1) - C(15)	3.056(2)	C(8) - H(2)	2.704(2)
O(2) - H(11)	2.585(2)	C(8) - H(15)	2.717(2)
O(2) - H(3)[a]	2.597(1)	C(9) - H(6)[d]	2.802(2)
O(2) - C(11)	2.836(3)	C(10) - H(2)[e]	2.982(2)
N(1) - H(2)	2.618(2)	C(12) - H(3)[e]	2.993(3)
N(2) - H(3)[b]	2.861(2)	C(15) - H(2)[e]	2.922(2)
C(4) - H(15)[c]	2.949(2)		

*Bond lengths corrected for riding motion, where the second atom is riding on the first.

[a]Atom located at position 1½-x, -½+y, ½-z.

[b]Atom located at position 1-x, 2-y, -z.

[c]Atom located at position -½+x, 2½-y, -½+z.

[d]Atom located at position 1-x, 2-y, 1-z.

[e]Atom located at position 2-x, 2-y, 1-z.

Table 13. Selected Bond Angles (deg) for $(PhCO)_2CN_2$.

BOND ANGLES

N(2)-N(1)-C(8)	175.8(2)	C(9)-C(10)-C(15)	122.5(2)
N(1)-C(8)-C(7)	116.4(2)	C(1)-C(2)-C(3)	120.0(2)
N(1)-C(8)-C(9)	111.4(2)	C(2)-C(3)-C(4)	120.2(2)
O(1)-C(7)-C(1)	121.3(2)	C(3)-C(4)-C(5)	120.2(2)
O(1)-C(7)-C(8)	120.3(2)	C(4)-C(5)-C(6)	120.1(2)
O(2)-C(9)-C(8)	119.9(2)	C(5)-C(6)-C(1)	120.2(2)
O(2)-C(9)-C(10)	121.2(2)	C(6)-C(1)-C(2)	119.1(2)
C(1)-C(7)-C(8)	118.4(2)	C(10)-C(11)-C(12)	120.2(2)
C(7)-C(8)-C(9)	130.5(2)	C(11)-C(12)-C(13)	120.0(2)
C(8)-C(9)-C(10)	118.8(2)	C(12)-C(13)-C(14)	120.4(2)
C(7)-C(1)-C(2)	121.7(2)	C(13)-C(14)-C(15)	120.0(2)
C(7)-C(1)-C(6)	119.2(2)	C(14)-C(15)-C(10)	120.2(2)
C(9)-C(10)-C(11)	118.2(2)	C(15)-C(10)-C(11)	119.2(2)

TORSION ANGLES

C(1)-C(7)-C(8)-N(1)	- 36.7
C(1)-C(7)-C(8)-C(9)	159.4(2)
O(1)-C(7)-C(8)-C(9)	- 20.7(3)
C(7)-C(8)-C(9)-O(2)	154.5(2)
C(7)-C(8)-C(9)-C(10)	- 27.9(3)
N(1)-C(8)-C(9)-C(10)	167.5(2)
O(2)-C(9)-C(10)-C(15)	148.2(2)
O(2)-C(9)-C(10)-C(11)	- 28.4(3)
C(8)-C(9)-C(10)-C(11)	154.1(2)
C(8)-C(9)-C(10)-C(15)	- 29.3(3)
C(2)-C(1)-C(7)-C(8)	- 30.4(3)
C(2)-C(1)-C(7)-O(1)	149.7(2)
C(6)-C(1)-C(7)-O(1)	- 28.4(3)
C(6)-C(1)-C(7)-C(8)	151.6(2)
O(2)-C(9)-C(8)-N(1)	- 10.0(3)
O(1)-C(7)-C(8)-N(1)	- 36.8(2)

DESCRIPTION OF STRUCTURE AND DISCUSSION

The unit cell of dibenzoyldiazomethane consists of four discrete molecules, with no unusually close intermolecular contacts. The molecule has an s-trans-s-cis configuration as initially proposed by Murai *et al*[4] based on e.s.r. results, but is in conflict with the s-cis-s-cis geometry proposed for the related diazoalkanes $RCOCN_2COR'$ ($R,R' = CH_3, C_2H_5, CH(CH_3)_2, C(CH_3)_3$) based on ^1H NMR spectra and dipole measurements.[5] While there is likely some cis-trans isomerization in solution, it is unlikely from steric arguments, that the s-cis-s-cis geometry would dominate, except possibly for the smallest substituents (R,R'). In the present structure however, the s-trans-s-cis geometry is consistent with such steric arguments, in that the two bulky phenyl groups have minimal contacts. The third possible conformation, s-trans-s-trans, would also minimize non-bonded contacts and in this regard, would seem to be the preferred conformation. For the s-trans-s-trans geometry, two carbonyl groups would have to be in close contact, whereas for the observed s-trans-s-cis conformation, one carbonyl and the much larger phenyl group are in close proximity. The observed geometry must therefore result from electronic factors (*vide infra*).

In the title compound, the close contacts between the carbonyl group and the phenyl ring, a consequence of the

s-trans-s-cis geometry, result in significant deviations from planarity within the molecule. The molecule is twisted about the C(7)-C(8) and C(8)-C(9) bonds such that O(1) is thrust above the diazomethylene plane while O(2) falls below this plane. The resulting O(1)-C(7)-C(8)-N(1) and O(2)-C(9)-C(8)-N(1) torsion angles are -36.8(2)° and -10.0(3)°, respectively. These molecular twists oppose the tendency for the diazo and ketone groups to be coplanar[3] and therefore reduce the π-delocalization somewhat. A tendency to maximize the delocalization probably keeps the molecule from deviating even more from planarity. Significantly, the cis carbonyl group (C(9)-O(2)) is twisted only 10° from the diazo group while the trans carbonyl (C(7)-O(1)) is twisted by *ca.* 37°. The latter group is the one interacting with the phenyl ring of the other benzoyl moiety in the present conformation. The two phenyl rings are also twisted by *ca.* 29° from the carbonyl groups, such that ring 1 (C(1)-C(6)) avoids the diazo group and ring 2 (C(10)-C(15)) avoids the carbonyl C(7)-O(1). This twisting also serves to reduce the possible delocalization over the molecular framework.

The C-C distances within both phenyl groups (average 1.385(8) and 1.381(6) Å) are somewhat shorter than in benzene and its derivatives,[13] but these values not unexpected from the thermal vibrations of the rings. Consistent with this argument, the shortest C-C distances occur at the far

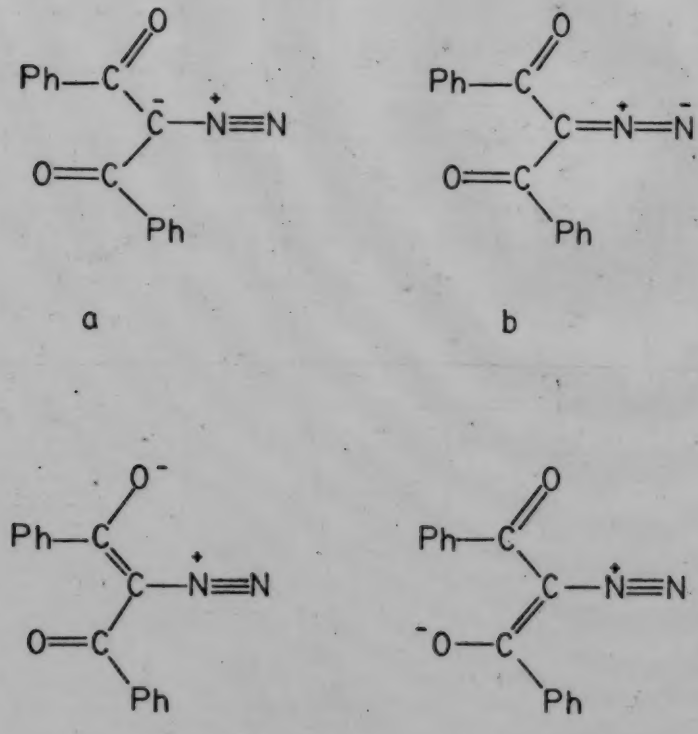
ends of the molecule (C(3),C(4),C(5) and C(12),C(13), C(14)) where the thermal motion is greatest. The C(1)-C(7) and C(9)-C(10) distances (1.488(2) and 1.487(3) Å, respectively) are in excellent agreement and correspond to normal C-C single bonds between sp^2 hybridized carbon atoms.[14] On the other hand the C(7)-C(8) and C(8)-C(9) distances (1.469(3) and 1.477(3) Å, respectively) are somewhat shorter, indicating partial double bond character. Both carbonyl C-O distances (1.224(2) for C(7)-O(1) and 1.221(2) Å for C(9)-O(2)) are in good agreement with each other and indicate normal C=O double bonds.[15] If these bond lengths are corrected for riding motion however, the corrected values (1.240(2) and 1.250(2) Å, respectively) indicate a bond order somewhat less than two, resulting from delocalization within the molecule. These corrected values may offer a better description of the carbonyl groups since they take the thermal vibrations of these groups into account.

Within the diazomethylene part of the molecule, the C-N-N angle is virtually linear (175.8(2)°), the C-N bond length (1.339(2) Å) indicates a partial double bond[16] and the N-N bond distance (1.112(2) Å) is very close to the triple bond values observed in dinitrogen and aromatic diazonium compounds (1.097-1.098 Å).[17,18] All three parameters agree well with the values reported for the six other diazoalkane molecules (C-N bond range 1.31-1.37 Å; N-N bond range 1.10-1.126 Å; N-N-C angle range 177°-180°).[19-24]

However, owing to thermal vibration, the N-N distance will be artificially short when an individual atom treatment is used and uncorrected values are not really meaningful. For this reason we prefer to rely on the riding motion corrected value. This value for the N-N distance (1.151(3) Å) is intermediate between a double and a triple bond,[25] consistent with the partial double bond character of the C-N bond, and again, indicates the electron delocalization within the molecule.

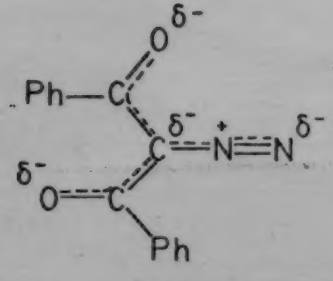
In order to establish the preference of the s-trans-s-cis conformation over the sterically favored s-trans-s-trans geometry, it is worthwhile considering some of the canonical forms possible for the molecule in the favored conformation, as shown in Figure 8. As mentioned previously, significant delocalization over the molecular framework is possible if all atoms are coplanar,[3] and this is clearly seen from the canonical forms in Figure 8. The planarity of the molecule is opposed, however, by steric interactions which tend to suggest instead that the s-trans-s-trans conformation is most likely. However the average structure 8e indicates an electrostatic stabilization for the observed conformation. This interaction results from the positive charge on N(1) and the negative charge on O(2). Consistent with this argument, the torsion angle involving the carbonyl cis to the diazo group, O(2)-C(9)-C(8)-N(1), is only 10° whereas for the trans carbonyl, where there is no such

Figure 8. Major Canonical Forms for the s-trans-s-cis Conformation of $PhCOCN_2COPh$.



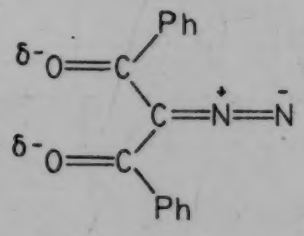
a b c d

Average Electron Density Distribution



e

stabilizing electrostatic attraction, the torsion angle, O(1)-C(7)-C(8)-N(1), is 37°. For an s-trans-s-trans geometry, there would be no attractive interactions possible between carbonyl and diazo groups, and in fact a destabilizing, repulsive interaction would result between the two carbonyl groups, as illustrated below.



Electrostatically, the s-cis-s-cis conformation is favored, whereas based on steric arguments, the s-trans-s-trans geometry is most likely. The observed s-trans-s-cis geometry is therefore a compromise between the electrostatic and steric forces within the molecule. The molecular parameters indicate that, in spite of the significant deviations from planarity, there is significant delocalization over the molecular framework. It should also be noted that the thermally corrected diazo and carbonyl bond lengths are those that are most chemically reasonable, giving the expected bond orders.

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Chapter IV.

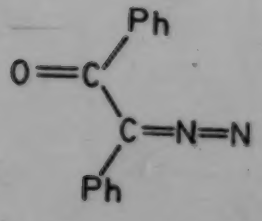
The Structure of Benzoylphenyldiazomethane.

INTRODUCTION

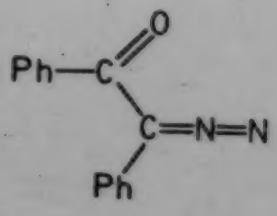
The e.s.r. spectrum of benzoylphenyldiazomethane, commonly known as azibenzil, has been reported by Murai, Torres and Strausz.[1] These authors noted that photolysis of a microcrystalline sample of $PhCOCN_2Ph$ at 77°K resulted in a complex e.s.r. spectrum, consisting of a strong and a weak triplet signal and a quintet signal. The strong triplet was assigned to the trans conformer of the benzoylphenylmethylene radical, which is formed through loss of N_2 from the starting diazoalkane molecule, also assumed to have the trans geometry in the solid state. The weak triplet was assigned to the presence of small amounts of the cis conformer of this radical, and the novel quintet state was attributed to a triplet-triplet radical pair formed by the pairwise interaction of two triplet state benzoylphenylmethylene radicals, each having a trans conformation. For such a radical pair to form, two radicals must be in close proximity in the crystal lattice, which could result if, in a crystal sample of the parent diazoalkane species, two molecules were oriented such that there were close interactions between the diazo functions. Since benzoylphenyldiazomethane forms a relatively stable crystalline product, similar to the related species $(PhCO)_2CN_2$ discussed

in Chapter III, a structural determination was undertaken to determine the intermolecular interactions within the unit cell in order to further understand the e.s.r. spectrum and to confirm the proposed trans geometry of the molecule.

Semiempirical CNDO/2 calculations[2] on benzoylphenyldiazomethane indicate that two geometries are preferred, having the carbonyl and diazo groups either cis or trans across the single bond, and having an essentially planar molecular framework. Other conformations resulting from rotations about the C-C bond were not favored.



trans



cis

However, the electric dipole moment measurements[3] are compatible with either two cis-trans conformers in equilibrium or with only a single skewed conformer. Therefore the structure of $PhCOCN_2Ph$ is also of interest for comparison with the results of the theoretical calculations.

In addition, the structural determination of benzoylphenyldiazomethane is of interest in relation to the structure of dibenzoyldiazomethane discussed in Chapter III. Few diazoalkane molecules have been structurally characterized[4-9] and in none of these reports have the structures been discussed in terms of thermally corrected bond lengths. We maintain that when the atoms are undergoing significant thermal vibration, as is often the case at room temperature, the thermally corrected bond lengths are often more meaningful than the uncorrected values obtained from the least squares analysis. This is clear in previous structures of diazoalkane molecules[4-9] where the C-N bond lengths indicated bond orders of *ca.* 1.5, whereas the corresponding N-N bond lengths were abnormally short, corresponding to bond orders close to 3, rather than the expected 2.5. We believe that this N-N bond shortening is a consequence of thermal vibration rather than increased N-N bond order as has previously been implied.[4] The suitably corrected structural parameters of $PhCOCN_2Ph$, are therefore important for comparison with the parameters of $(PhCO)_2CN_2$, which have been handled in an analogous manner, to help establish structural and chemical trends within diazoalkane molecules.

EXPERIMENTAL

Orange needles of benzoylphenyldiazomethane recrystallized from ether, were kindly supplied by Dr. M. Torres

and Professor O.P. Strausz (University of Alberta). A suitable crystal fragment, cut from one of the needles, was mounted in the air on a glass fibre. Preliminary film data showed Laué symmetry mmm with systematic absences ($h00$, $h = 2n+1$; $0k0$, $k = 2n+1$; 00ℓ, $\ell = 2n+1$) consistent with the space group $P2_12_12_1$. The cell parameters, along with the pertinent crystal data and intensity collection details are listed in Table 14. Otherwise the data collection proceeded as outlined in Chapter II.

STRUCTURE SOLUTION AND REFINEMENT

The structure was solved by direct methods using the program MULTAN .[10] The solution was based on 300 reflections having $|E| > 1.03$ and 2000 phase relationships. The E-map corresponding to the solution with the best combined figure of merit yielded the positions of all non-hydrogen atoms. All hydrogen atoms were found in a subsequent electron density difference map phased on the heavier atom framework. Full matrix least-squares techniques were used, with atomic scattering factors from Cromer and Waber[11] used for all atoms except hydrogen, for which the values from Stewart, Davidson and Simpson[12] were used. Anomalous dispersion terms for O, N and C were included in F_c. All non-hydrogen atoms were refined as individual atoms, with the phenyl carbon atoms having isotropic thermal parameters, and the rest having anisotropic thermal parameters. The hydrogen atoms were included as fixed contributions in

Table 14. Summary of Data and Intensity Collection for Benzoylphenyldiazomethane.

Compound	$(C_6H_5)COCN_2(C_6H_5)$
Formula	$C_{14}H_{10}N_2O$
Formula Weight	222.25
Cell Parameters	
a	5.600(1) Å
b	13.347(2) Å
c	15.018(3) Å
V	1122.5
Z	4
Density	1.315 $g \cdot cm^{-1}$ (calcd.) 1.30(1) $g \cdot cm^{-1}$ (exptl., floatation)
Space Group	$D_2^4 - P2_12_12_1$
Crystal Dimensions	0.384 x 0.216 x 0.129 mm
Crystal Volume	0.0107 mm^3
Crystal Shape	orthorhombic prism with faces $0\bar{1}\bar{1}$, 011, $0\bar{1}2$, $01\bar{2}$, 100, $\bar{1}00$
Temperature	20°C
Radiation	Cu Kα (λ = 1.540562 Å)
μ	6.447 cm^{-1}
Receiving Aperture	4mm x 4mm; 30 cm from the crystal
Takeoff Angle	5.50°
Scan Speed	2° in 2θ/min
Scan Range	1.0° below $K\alpha_1$ to 1.0° above $K\alpha_2$
Background Counting Time	20 s

Table 14, Continued

2θ Limits	3.0°- 123°
2θ Limits for Centered Reflections	$50.0° \leq 2\theta \leq 70°$
Final Number of Parameters	94
Unique Data Collected	1068
Unique Data Used ($F_o^2 \geq 3\sigma(F_o^2)$)	888
Error in Observation of Unit Weight	1.979 electrons
R	0.052
R_w	0.070

their idealized positions, with thermal parameters of 1 $\mathring{A}^2$ greater than the equivalent isotropic B for the corresponding carbon atom. Absorption corrections were not applied owing to the very small magnitude of the linear absorption coefficient (6.447 cm^{-1}). In the final electron density difference map, the top twenty residuals ranged from 0.31 to 0.14 $e/\mathring{A}^3$, and were in the vicinity of the two phenyl rings. In earlier difference Fourier maps, a typical hydrogen atom had an electron density of about 0.27 $e/\mathring{A}^3$. For a more detailed discussion of structure solution techniques, the reader is referred to Chapter II.

RESULTS

A stereoview of the unit cell is shown in Figure 9. The crystallographic *a* axis goes into the page, the *b* axis runs from top to bottom and the *c* axis is from right to left. Figure 10 (50% ellipsoids) indicates the numbering scheme used within the molecule (hydrogen atoms have the same number as their attached carbon atoms). The final positional and thermal parameters for the non-hydrogen atoms are listed in Table 15 and the idealized positional and thermal parameters for the hydrogen atoms are given in Table 16. Selected interatomic distances are listed in Table 17, while bond angles and torsion angles are presented in Table 18. The least squares plane calculations are recorded in Table 19. A listing of the observed and calculated structure amplitudes is available.[13]

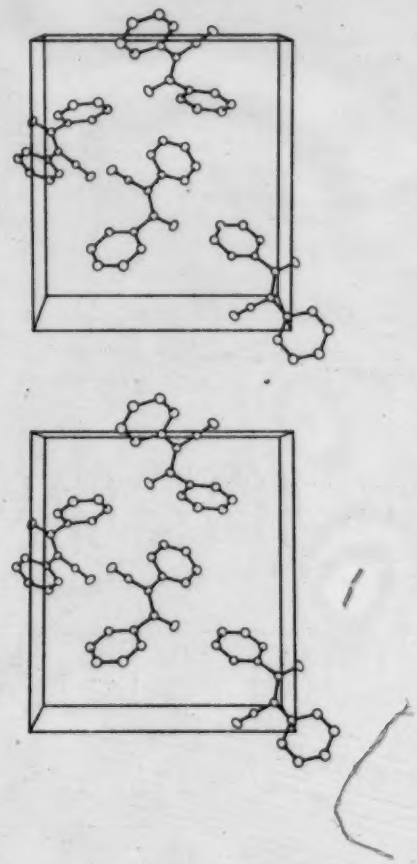


Figure 9. Cell Packing Diagram of $PhCOCN_2Ph$.

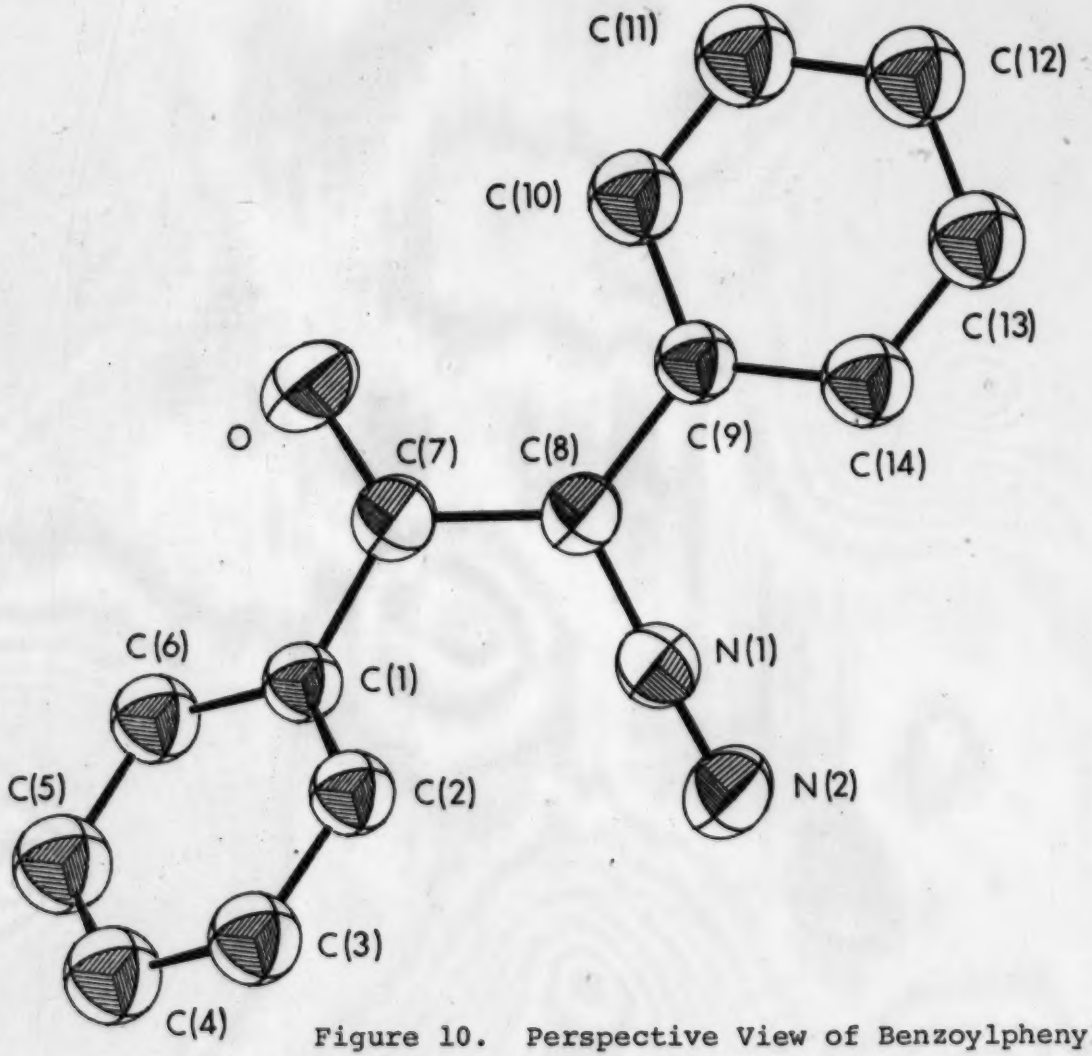


Figure 10. Perspective View of Benzoylphenyldiazomethane.

Table 15. Positional and Thermal Parameters For the Non-Hydrogen Atoms of [PhCOCN2Ph].

Atom	x[a]	y	z	U11[b]	U22	U33	U12	U13	U23
(O)	0.4289(7)	0.5492(2)	0.6751(2)	8.4(2)	4.6(2)	6.8(2)	-1.4(2)	1.8(2)	-1.5(2)
N(1)	0.4459(7)	0.3658(2)	0.5107(2)	5.4(2)	4.3(2)	4.6(2)	-0.4(2)	0.3(2)	0.2(2)
N(2)	0.3788(8)	0.3005(3)	0.4698(2)	7.3(3)	5.5(2)	5.8(2)	-1.3(2)	0.5(2)	-1.3(2)
C(7)	0.4017(8)	0.4677(3)	0.6379(3)	4.8(2)	3.6(2)	5.2(2)	0.1(2)	0.1(2)	-0.1(2)
C(8)	0.5268(8)	0.4447(3)	0.5552(3)	5.2(3)	3.4(2)	4.4(2)	-0.2(2)	0.2(2)	-0.2(2)
C(1)	0.2444(7)	0.3909(3)	0.6795(2)	0.51(1)[c]					
C(2)	0.3141(8)	0.2906(3)	0.6874(3)	3.65(8)					
C(3)	0.1689(9)	0.2232(3)	0.7328(3)	4.36(9)					
C(4)	-0.043(1)	0.2540(3)	0.7685(3)	4.8(1)					
C(5)	-0.1113(9)	0.3538(4)	0.7615(3)	4.9(1)					
C(6)	0.0323(9)	0.4214(3)	0.7184(3)	3.98(9)					
C(9)	0.7246(8)	0.5007(3)	0.5126(3)	3.36(8)					
C(10)	0.7805(9)	0.5975(3)	0.5381(3)	4.38(9)					
C(11)	0.972(1)	0.6464(4)	0.4985(3)	5.0(1)					
C(12)	1.102(1)	0.6020(3)	0.4324(3)	4.8(1)					
C(13)	1.0466(9)	0.5068(3)	0.4058(3)	4.57(9)					
C(14)	0.8591(9)	0.4564(3)	0.4464(3)	4.21(9)					

[a] Estimated standard deviations in the least signicant figure(s) are given in parentheses in this and all subsequent tables.

[b] The form of the thermal ellipsoid is: $\exp[-2\pi^2(a^{*2}U11h^2+b^{*2}U22k^2+c^{*2}U33l^2+2a^*b^*U12hk+2a^*c^*U13hl+2b^*c^*U23kl)]$. The quantities given in the table are the thermal coefficients x 10^2.

[c] Isotropic B(A^2).

Table 16. Idealized Positional and Thermal Parameters For the Hydrogen Atoms of [PhCOCN2Ph].

Atom	x	y	z	B(A²)	Atom	x	y	z	B(A²)
H(2)	0.4602	0.2686	0.6619	4.65	H(10)	0.6882	0.6304	0.5824	5.38
H(3)	0.2176	0.1554	0.7392	5.36	H(11)	1.0135	0.7120	0.5177	5.99
H(4)	-0.1437	0.2072	0.7979	5.80	H(12)	1.2307	0.6370	0.4051	5.84
H(5)	-0.2580	0.3753	0.7868	5.93	H(13)	1.1358	0.4754	0.3598	5.58
H(6)	-0.0140	0.4898	0.7151	4.98	H(14)	0.8225	0.3900	0.4282	5.21

Table 17. Selected Interatomic Distances (Å) for $PhCOCN_2Ph$.

BONDED CONTACTS

N(1)-N(2)	1.130(5)	C(3)-C(4)	1.365(7)
N(1)-N(2)*	1.151(5)	C(4)-C(5)	1.390(7)
N(1)-C(8)	1.328(5)	C(5)-C(6)	1.372(6)
C(7)-O	1.231(4)	C(6)-C(1)	1.385(6)
C(7)-O*	1.257(5)	C(9)-C(10)	1.383(6)
C(1)-C(7)	1.489(5)	C(10)-C(11)	1.390(7)
C(7)-C(8)	1.459(6)	C(11)-C(12)	1.367(7)
C(8)-C(9)	1.482(6)	C(12)-C(13)	1.367(6)
C(1)-C(2)	1.399(5)	C(13)-C(14)	1.389(7)
C(2)-C(3)	1.391(6)	C(14)-C(9)	1.381(6)

NON-BONDED CONTACTS

O-H(10)	2.285(3)	C(8)-H(14)	2.630(4)
O-C(6)	2.874(5)	C(8)-H(10)	2.669(4)
O-C(10)	2.920(6)	C(3)-H(14)[a]	2.978(5)
N(1)-H(14)	2.467(4)	C(12)-H(5)[e]	2.931(5)
N(1)-H(2)	2.617(3)	C(13)-H(5)[e]	2.877(5)
N(1)-C(14)	2.783(6)	C(13)-N(1)[d]	3.320(6)
N(2)-N(2)[a,b]	3.238(4)	C(13)-N(2)[d]	3.459(6)
N(2)-N(1)[a]	3.300(6)	H(14)-C(2)[b]	2.971(4)
C(7)-H(6)	2.617(4)	H(14)-C(3)[b]	2.978(5)
C(7)-H(2)	2.702(4)	O-C(8)[c]	5.541(6)
C(8)-C(8)[a,b]	6.133(6)	O-C(8)[f]	6.254(5)
C(8)-C(8)[c,d]	5.600(1)		

*Bond lengths corrected for riding motion, where the second atom is riding on the first.

[a]Atom is located at the position $-\frac{1}{2}+x, \frac{1}{2}-y, 1-z$.

[b]Atom is located at the position $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$.

[c]Atom is located at the position $-1+x, y, z$.

[d]Atom is located at the position $1+x, y, z$.

[e]Atom is located at the position $\frac{1}{2}-x, 1-y, -\frac{1}{2}+z$.

[f]Atom is located at the position $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$.

Table 18. Selected Angles (deg) for $PhCOCN_2Ph$.

BOND ANGLES

N(2)-N(1)-C(8)	177.3(4)	C(1)-C(2)-C(3)	119.8(4)
N(1)-C(8)-C(7)	115.6(4)	C(2)-C(3)-C(4)	120.4(4)
N(1)-C(8)-C(9)	116.0(4)	C(3)-C(4)-C(5)	119.8(5)
O-C(7)-C(8)	120.8(4)	C(4)-C(5)-C(6)	120.3(5)
O-C(7)-C(1)	119.4(4)	C(5)-C(6)-C(1)	120.5(4)
C(1)-C(7)-C(8)	119.7(3)	C(6)-C(1)-C(2)	119.0(4)
C(7)-C(8)-C(9)	128.4(3)	C(9)-C(10)-C(11)	119.6(4)
C(7)-C(1)-C(2)	122.0(4)	C(10)-C(11)-C(12)	121.3(4)
C(7)-C(1)-C(6)	118.7(3)	C(11)-C(12)-C(13)	119.6(5)
C(8)-C(9)-C(10)	121.4(4)	C(12)-C(13)-C(14)	119.7(5)
C(8)-C(9)-C(14)	120.2(4)	C(13)-C(14)-C(9)	121.4(4)
		C(14)-C(9)-C(10)	118.5(4)

TORSION ANGLES

C(1)-C(7)-C(8)-N(1)	16.3(6)
C(1)-C(7)-C(8)-C(9)	-166.8(4)
O-C(7)-C(8)-C(9)	11.4(7)
O-C(7)-C(8)-N(1)	14.5(4)
C(7)-C(8)-N(1)-N(2)	143 (10)
C(10)-C(9)-C(8)-N(1)	- 18.1(4)
C(2)-C(1)-C(7)-O	46.3(4)

Table 19. Least Squares Plane Calculations.[a]

plane no.	equation
1	-0.6487X + 0.5856Y - 0.4861Z + 2.4715 = 0
2	-0.7752X + 0.3628Y - 0.5171Z + 4.4422 = 0
3	-0.4739X - 0.2080Y - 0.8557Z + 10.4751 = 0
4	-0.6247X + 0.3666Y - 0.6894Z + 5.3887 = 0

Deviations from the Planes (Å)

Atom	Plane no. 1	2	3	4
O	0.277(3)[b]	-0.003(3)		
N(1)	-0.017(4)			
N(2)	0.015(4)			
C(1)		-0.003(4)	0.010(4)	
C(2)			0.001(4)	
C(3)			-0.010(5)	
C(4)			0.009(5)	
C(5)			0.002(5)	
C(6)			0.012(4)	
C(7)	0.011(4)	0.009(4)	-0.087(4)[b]	
C(8)	-0.019(4)	-0.003(4)		-0.026(4)[b]
C(9)	0.011(4)			-0.004(4)
C(10)				0.011(5)
C(11)				-0.010(5)
C(12)				0.002(5)
C(13)				0.006(5)
C(14)				-0.005(5)

Dihedral Angles Between Planes

Plane A	Plane B	angle(deg)
1	2	14.8
1	3	53.0
1	4	17.2
2	3	42.7
2	4	13.1
3	4	35.9

[a] X, Y, and Z are the orthogonal coordinates (Å) with X along the a axis, Y in the (a-b) plane and Z along the c^* axis.

[b] Not included in the least squares plane calculation.

DESCRIPTION OF STRUCTURE AND DISCUSSION

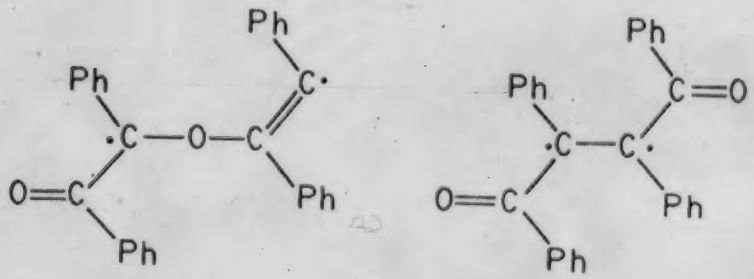
Within the unit cell of benzoylphenyldiazomethane there are four discrete molecules. Figure 9 indicates that these molecules can be grouped in pairs along the crystallographic screw axis in the x-direction. In this arrangement the molecules have their diazomethylene groups directed towards each other but inclined somewhat along a such that zig-zag arrays of diazomethylene groups, parallel to the a axis, result. These diazomethylene groups therefore come into rather close contact, and the N(2)-N(2) distance along the zig-zag chain is 3.238(4) Å. Although it is difficult to establish a normal van der Waals contact for such an interaction, this contact can be related to the radius of an aromatic ring (1.85 Å).[14] It is not unreasonable to assume that the π system of the diazomethylene function is similar to that of an aromatic ring, and thus we estimate that a normal non-bonded contact between two diazo functions is approximately 3.70 Å. As such, the N(2)-N(2) distance in the present structure indicates a significant interaction between the two diazomethylene groups.

In the e.s.r. study by Strausz and coworkers,[1] photolysis of a microcrystalline sample of the title compound at 77°K resulted in the production of the benzoylphenylmethylene radical. Since the elimination of N_2 at this temperature in the solid state is not expected to change

the geometry of the molecule, the cell packing diagram shown in Figure 9 should be representative of the orientation of the radicals after photolysis and should prove useful in interpreting the e.s.r. results. Initially, the e.s.r. spectrum showed a strong triplet signal (assigned to the trans configuration of the benzoylphenylmethylene radical), a weak triplet signal (assigned to the cis configuration of this group) and a quintet signal. The quintet signal was thought to arise from the pairwise interaction of two neighboring triplet radicals.[1] Within the unit cell of benzoylphenyldiazoalkane, there are two close contacts between neighboring carbene carbon atoms which could give rise to this interaction. The first is along the zig-zag chain, where the C(8)-C(8) separation is 6.133(6) Å, and the second occurs between molecules separated by one unit cell translation in *a*, in which the C(8)-C(8) distance is 5.600(1) Å. Both possibilities are consistent with the separation expected between radical pairs producing the quintet signal, as indicated by the zero field splitting parameter, D(0.0943 cm^{-1}),[1] which is a function of the separation of unpaired electrons in the radicals.

Upon warming the benzoylphenylmethylene radical from 77°K to 90°K, the quintet signal decays to a new triplet signal which was postulated to result from the formation of a diradical through inversion and a single, covalent bond formation.[1] This new triplet signal, which decays

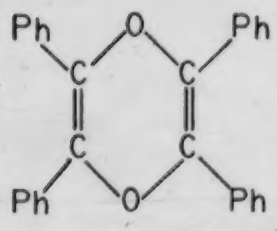
above 120°K could result from a covalent bond formed between the carbene carbon atom of one molecule and a carbonyl linkage of another (as in (a) below), or between the carbene atoms of two adjacent molecules, resulting in (b).[15]



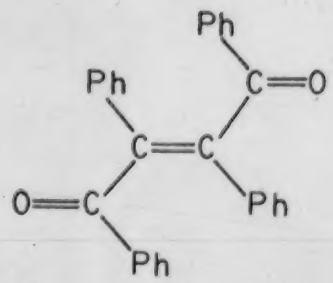
a b

The closest contacts of type (a) occur between molecules separated by one cell translation along the *a* axis, where the C(8)-O distance is 5.541(6) Å. The next closest such interaction is 6.254(5) Å (see Table 17). The two closest interatomic distances between carbene atoms C(8)-C(8) are 5.600(1) and 6.133(6) Å (*vide supra*). It is not possible to determine which bond formation is most likely from the structural data. However, if a C(8)-O bond is formed, the decay of the triplet signal (above 120°K) may result from rearrangement of the molecule and formation of another bond, resulting in (c).[15] In the case of a

C(8)-C(8) bond formation, this decay could result from a rotation about the C(8)-C(8) bond, with the subsequent formation of a C=C double bond, as in (d).[15]



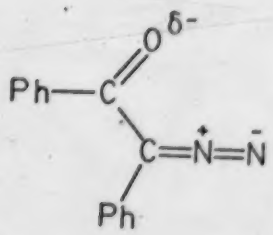
c



d

Within the molecule, the carbonyl and diazo groups are trans to each other across the C-C single bond, as expected from the e.s.r. results.[1] This geometry and the cis conformation are the two which are favored owing to π-delocalization within the molecule, and theoretical calculations[2] on benzoylphenyldiazomethane have confirmed this. The preference of one of these two conformations over the other is dependent on several factors, as discussed in Chapter III. For optimum delocalization of the π electrons, the whole molecular fragment should be planar.[16] This planarity is opposed by steric interactions, the greatest of which occurs between the two phenyl groups in the cis configuration. Thus, the two phenyl rings cannot both be coplanar with the carbonyl and diazo groups, and delocaliz-

ation through the phenyl rings is lost in this conformation. However, as shown in Chapter III, the cis conformation is stabilized by an electrostatic attraction between the carbonyl and diazo functions, which is not possible in a trans geometry.



Which of the two preferred conformations is favored will depend on which of the above stabilizing or destabilizing forces predominate. In the present compound, the observed trans geometry implies that the steric repulsion between the two phenyl groups predominate, and thus the trans configuration is preferred. It is also possible that the observed trans conformer may be favored in the present structure by packing considerations.

In the trans conformation, the molecule is most stable when it is completely planar, owing to the possibility of π-delocalization.[16] However, in the present structure, the molecule is not totally planar, but is skewed somewhat. For example, the O-C(7)-C(8)-N(1) torsion angle is 14.5(4)°

and the torsion angle between phenyl ring 2 and the diazomethane group (C(10)-C(9)-C(8)-N(1)) is -18.1(4)°. These two values indicate that some conjugation is possible between the carbonyl and diazo group and between the diazo group and the adjacent phenyl ring. On the other hand the C(1)-C(6) phenyl ring is twisted considerably from the adjacent carbonyl group (torsion angle C(2)-C(1)-C(7)-O = 46.3(4)°), allowing very little electron delocalization between this phenyl and the carbonyl group. This twisting probably results from steric interactions between the phenyl ring and the diazo and carbonyl groups, with the phenyl rings skewing to avoid contacts with these groups.

The C-C distances within ring 1 (C(1)-C(6), average 1.384(12) Å) and ring 2 (C(9)-C(14), average 1.378(8) Å), analogous to those in dibenzoyldiazomethane, are somewhat shorter than the values found in benzene and its derivatives.[17] Again, this is consistent with the thermal vibrations of the rings, with the shortest C-C distances occurring at the C(4) and C(12) ends of the rings, where the thermal motion is the greatest. The C(1)-C(7) and C(8)-C(9) distances (1.489(5) and 1.482(6) Å) agree well with the predicted value for a single bond between sp^2 hybridized carbon atoms,[14] indicating that there is little actual delocalization between either of the phenyl rings and the carbonyldiazo backbone, even though some conjugation is possible between ring 2 and the diazo group (*vide supra*). The C(7)-

C(8) bond length (1.459(6) Å), on the other hand, is intermediate between a single and double bond,[14] and suggests significant conjugation between the carbonyl and diazo functions. In dibenzoyldiazomethane, the corresponding bond lengths (1.469(3) and 1.477(3) Å) are somewhat longer than in the present structure, although not significantly. In addition, the carbonyl C(7)-O distance in the present structure (1.231(4) Å) although not significantly different from the two carbonyls in $(PhCO)_2CN_2$ (1.224(2) and 1.221 (2) Å), is still somewhat longer. Although the differences for the C-C and C-O bond lengths between the mono and dibenzoyl compounds are not significant, taken together, they are consistent with a somewhat higher degree of conjugation between the diazo and carbonyl groups in the present structure, possibly because the delocalization occurs over one carbonyl group in $PhCOCN_2Ph$, and over two in $(PhCO)_2CN_2$. A riding motion correction of the C-O bond yields a value of 1.257(5) Å, which indicates a bond order somewhat less than two.[18]

The diazomethylene fragment of the present structure is virtually linear (177.3(4)°), as expected. The N(1)-N(2) (uncorrected) bond length (1.130(5) Å) is somewhat longer than in the other reported diazoalkane structures,[4-9] where a range of 1.10(2) - 1.126(4) Å was observed. The N-N bond length corrected for riding motion (1.151(5) Å) is in excellent agreement with the analogous thermally corrected

distance in dibenzoyldiazomethane (1.151(3) Å) and indicates a bond order of *ca.* 2.5.[19] Again, the corrected bond distance is believed to be a better indication of the true bond length, since thermal motion is taken into account. Furthermore, this corrected distance corresponds to the expected N-N bond order. The C(8)-N(1) bond length of 1.328(5) Å is somewhat shorter than the corresponding value in dibenzoyldiazomethane (1.339(2) Å), and is intermediate between a single and double bond.[20] The N-N and C-N bond distances are consistent with a significant amount of π-delocalization within the diazomethylene group, and again suggest that the delocalization in the present structure is somewhat greater than in the dibenzoyl species.

Overall, these structural parameters of benzoylphenyldiazomethane indicate there is a considerable amount of conjugation between the carbonyl and diazo groups, as predicted by the theoretical model.[2] It should be noted however, that in the theoretical model, the parameters used suggested the presence of more delocalization than was actually observed. Based on the structural parameters, for example, there is very little, if any, delocalization between the phenyl rings and either the carbonyl or the diazo group, even for ring 2 (C(9)-C(14)) which is only 17.2° out of the C(7)-C(8)-C(9)-N(1)-N(2) plane. This is not expected based on the theoretical calculations,[2] and, for ring 2 at least, cannot be attributed solely to

steric interactions, which would force the rings to adopt a non-planar conformation in relation to the diazoalkane backbone.

The title complex is comparable to dibenzoyldiazomethane in many of its bonding parameters, although there appears to be more conjugation between the carbonyl and diazo groups in the monobenzoyl compound compared to the dibenzoyl compound.

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Chapter V.

The Chemistry of Dibenzoyldiazomethane with Various Rh and Ir Complexes, and the Structure of $[IrCl((C_6H_4)COC(Ph)OPPh_2)(PPh_3)]\cdot C_6H_5CH_3$.

INTRODUCTION

Metal complexes containing the intact diazoalkane molecule are extremely rare, as outlined in Chapter I. The few such compounds which have been structurally characterized, however, show the variety of ways in which the diazoalkane molecule can coordinate to a metal centre. The aliphatic diazo molecule has been shown to coordinate end-on, through the terminal nitrogen atom;[1,2] side-on, through both nitrogen atoms;[3] through the diazo carbon atom, as a metallated diazoalkane;[4,5] and bridging two or more metal centres.[6,7] One of the reasons for the paucity of metal-diazoalkane complexes, with the diazoalkane ligand intact, is the reactivity of the diazo group.[8] The diazoketone compounds, $(PhCO)_2CN_2$ and $PhCOCN_2Ph$, described in Chapters III and IV, are of interest in this regard, since they are relatively stable molecules owing to π-delocalization through the α-ketone groups within both molecules. As such, it was hoped that reaction of these diazoketones with metal complexes would result in complexes having the diazoalkane function intact and bonded to the metal centre. Both diazoketone molecules may coordinate to a metal complex in

a variety of ways, in addition to the four bonding modes already observed in diazoalkane complexes (*vide supra*). They can be bound through the carbonyl groups alone, or chelating through the carbonyl groups and the diazo functions. In addition they can also undergo N_2 loss, resulting in the formation of carbenes, which may then be followed by ligand rearrangement as in other diazoalkane reactions.[9] The chemistry of dibenzoyldiazomethane with several rhodium and iridium complexes was therefore investigated in order to characterize some of the potentially interesting chemistry of this molecule.

EXPERIMENTAL

All manipulations were normally carried out under an atmosphere of dinitrogen and all solvents were dried and degassed prior to use. $IrCl_3 \cdot H_2O$ and $RhCl_3 \cdot 3H_2O$ were purchased from Research Organic/Inorganic Chemical Corporation; triisopropylphosphine was purchased from Strem Chemicals, and triphenylphosphine (Aldrich Chemicals) was recrystallized from ethanol prior to use. All other chemicals were reagent grade and used as obtained. Infrared spectra were recorded on either a Perkin Elmer Model 467 spectrometer using Nujol mulls on KBr plates; or a Nicolet 7199 F.T. interferometer using a CH_2Cl_2 film cast on KBr plates. NMR spectra were recorded on a Bruker HFX-90 NMR spectrometer. Mircoanalysis were performed by Canadian Microanalytical Service Ltd., Vancouver.

PREPARATION OF $[IrCl(CO)(PPh_3)_2]$

Two methods were used, a literature preparation by Collman *et al.*[10] and the one described below,[11] which yields a product freer from contaminants. $[IrCl(C_8H_{12})]_2$ [12] (1.0 g, 1.49 mmol) was placed in a 3 necked flask flushed with $N_2(g)$. 25 mL CH_2Cl_2 was added, followed by a stream of CO(g), at which time the solution turned black. Triphenylphosphine (1.56 g, 6.0 mmol dissolved in 25 mL of toluene) was added and the solution slowly turned red. Over two days the solution turned yellow and yielded a yellow precipitate. On addition of 30 mL of methanol, yellow crystals quickly precipitated from the remaining yellow solution. These crystals were air filtered and dried. Their infrared spectrum showed a single sharp band at 1960 cm^{-1}.

PREPARATION OF $[RhCl(PPh_3)_2]_2$

1.0 g of $[RhCl(C_8H_{12})]_2$ [13] (2.03 mmol) and 2.18 g of PPh_3 (8.31 mmol) were placed in a 3 necked flask with 50 mL toluene. The yellow solution turned salmon pink after stirring for 24 h. The precipitate was allowed to settle and the solvent removed. The product was stored under N_2 in the refrigerator at 2°C. The $^{31}P\{^1H\}$ NMR spectrum[14] of the product showed two species (~1:1 ratio): $[RhCl(PPh_3)_3]$ ($\delta_1 = 47.8$ ppm, doublet of triplets, $|^1J_{Rh-P}| = 191.7$ Hz,

$|^2J_{P-P}| = 38.8$ Hz; $\delta_2 = 31.7$ ppm, doublet of doublets, $|^1J_{Rh-P}| = 143.9$ Hz, $|^2J_{P-P}| = 38.8$ Hz) and $[RhCl(PPh_3)_2]_2$ ($\delta = 31.3$, doublet, $|^1J_{Rh-P}| = 150.2$ Hz).

REACTION OF $[IrCl(N_2)(PPh_3)]$ AND $(PhCO)_2CN_2$

0.16 g of $[IrCl(N_2)(PPh_3)_2]$[15] (2.05×10^{-1} mmol) and 0.056 g of $(PhCO)_2CN_2$ (2.2×10^{-1} mmol) were placed in a 3 necked round-bottom flask, and 10 mL of CH_2Cl_2 was added. The yellow solution turned dark green-brown immediately, with gas evolution. After 48 h, the solution was dark red-gold. This slowly lightened to yellow after two weeks. A yellow crystalline product (1) was isolated in varying yields (up to 30%) upon cooling to 2°C. The pertinent spectral results are: Infrared, 1954 cm^{-1}; $^{31}P\{^1H\}$ NMR, $\delta = -13.4$, singlet; mass spectrum, 974 (highest peak), 262 (base peak), 224 and 223 m/e. The $^{31}P\{^1H\}$ NMR of the reaction solution indicated, in addition to the resonance for 1, seven other unidentified species.

REACTION OF $[IrCl(CO)(PPh_3)_2]$ WITH $(PhCO)_2CN_2$

0.10 g of $[IrCl(CO)(PPh_3)_2]$ (1.28×10^{-1} mmol) and 0.035g of the diazoalkane (1.41×10^{-1} mmol) were mixed as solids and 10 mL of toluene was added. There was no apparent reaction and the yellow suspension was stirred for one week. A yellow solid isolated at that time was found to be the starting iridium carbonyl complex. No reaction product was observed or isolated.

REACTION OF $[IrCl(C_8H_{14})_2]_2$ WITH PPh_3 AND $(PhCO)_2CN_2$

0.16 g of $[IrCl(C_8H_{14})_2]_2$ [12] (1.79×10^{-1} mmol), 0.248 g of PPh_3 (9.4×10^{-1} mmol) and 0.13 g of $(PhCO)_2CN_2$ (5.20×10^{-1} mmol) were mixed as solids in a reaction flask and 10 mL of toluene was added. The solution turned black immediately, with the evolution of a gas. After 24 h, the solution was a dark red-gold color, and after two weeks, lightened to a yellow-red. The solution infrared and $^{31}P\{^1H\}$ NMR spectra indicated a mixture of species. One product precipitated as gold triclinic crystals (2) after standing at room temperature for two weeks (10% yield). The infrared spectrum showed major bands at 1636, 1577 and 1546 cm^{-1}, major peaks in the mass spectrum occurred at 974 (highest), 262 (base), 201 and 183 m/e, and the density of 2 was 1.47(1) $g \cdot cm^{-3}$. Although there was insufficient material for further characterization by NMR spectra or microanalysis, an X-ray structure of (2) was carried out (*vide infra*). No other products were characterized.

REACTION OF $[RhCl(C_8H_{14})_2]_2$ WITH PPh_3 AND $(PhCO)_2CN_2$

0.15 g of $[RhCl(C_8H_{14})_2]_2$ [16] (2.2×10^{-1} mmol), 0.315 g of PPh_3 (1.2 mmol) and 0.16 g of $(PhCO)_2CN_2$ (6.4×10^{-1} mmol) were reacted in 10 mL of toluene, as for the analogous Ir reaction. The solution turned dark red immediately, with gas evolution. After several hours, the solution was orange with an orange microcrystalline preci-

pitate (3). The isolated solid had infrared bands at 1675, 1625 and 1605 cm^{-1}, a singlet in the $^{31}P\{^{1}H\}$ NMR spectrum at 23.3 ppm, major peaks in the mass spectrum at 446 (highest), 262, 224, 223 and 105 (base) m/e and a melting point of 138°C. The elemental analysis of the orange product was consistent with the formulation $(Ph_3)PN_2C(COPh)_2$. Analysis: calcd. for $P_1O_2N_2C_{33}H_{25}$, 6.05% P, 6.25% O, 5.47% N, 77.34% C, 4.88% H; found 6.38% P, 6.20% O, 5.45% N, 77.25% C, 4.85% H. If the orange solution was allowed to sit at room temperature for several weeks, a white crystalline material (4) appeared, in small quantities. This compound showed a singlet in the ^{31}P NMR at 18.2 ppm; infrared bands at 1610, 1590, 1580 and 1530 cm^{-1}, major peaks in the mass spectrum at 484 (parent peak), 277 and 91 (base peak) m/e, and a melting point of 185°C.

REACTION OF $[IrCl(C_8H_{14})_2]_2$ WITH $P(i\text{-}C_3H_7)_3$ AND $(PhCO)_2CN_2$

0.10 g of the Ir complex, (1.12×10^{-1} mmol) was dissolved in 10 mL toluene and 0.18 g of the phosphine (1.12 mmol) was added. After 2 h, 0.075 g of the diazoalkane (3.0×10^{-1} mmol) was introduced through a sidearm attachment, and the orange solution turned a dark red-yellow with gas evolution. After standing for several weeks, a yellow crystalline product (5) was isolated, which had peaks in the infrared spectrum at 1675, 1610, 1600 and 1575 cm^{-1}; a singlet, ($\delta = 51.2$ ppm) in the $^{31}P\{^{1}H\}$ NMR spectrum; and

major peaks in the mass spectrum at 326 (highest), 325 (base), 160 and 105 m/e; a density of 1.178 g/ml; and a melting point of 108°C. Element analysis agreed with the forumlation $(i\text{-}C_3H_7)_3P{=}N_2C(COPh)_2$. Analysis: calcd. for $P_1O_2N_2C_{24}H_{31}$, 7.80% O, 6.83% N, 70.24% C, 7.56% H; found 7.52% O, 6.84% N, 70.09% C, 7.80% H.

REACTION OF $[RhCl(PPh_3)]_2$ AND $[RhCl(PPH_3)_3]$ WITH $(PhCO)_2CN_2$

0.10 g of the mixture of $[RhCl(PPh_3)_2]_2$ and $[RhCl(PPh_3)_3]$ and 0.41 g $(PhCO)_2CN_2$ (1.64×10^{-1} mmol) were mixed together and 10 mL CH_2Cl_2 was added. The solution immediately turned dark red-orange, and then became light orange with slow gas evolution, over a few minutes. $^{31}P\{^1H\}$ NMR spectra of the solution indicated initially the presence of two new species ($\delta_1 = 24.8$ ppm, doublet, $|^1J_{Rh-P}| = 117$ Hz; $\delta_2 = 18.2$ ppm, singlet) along with $[RhCl(PPh_3)_2]_2$ ($\delta = 31.3$, doublet, $|^1J_{Rh-P}| = 150.3$ Hz). After 24 h, only the singlet and $[RhCl(PPh_3)_2]_2$ resonances were observed.

X-RAY DATA COLLECTION

A crystal of 2 was mounted on a glass fibre. Preliminary film data showed Laué symmetry $\bar{1}$, with no systematic absences, consistent with the space groups P1 and $P\bar{1}$. The space group was determined to be P1 as was verified by the successful refinement of the structure with acceptable positional parameters, thermal parameters and agreement indices, and by the location of all phenyl hydrogens in

electron density difference maps. A cell reduction[17] failed to show the presence of higher symmetry. The reduced cell parameters along with the pertinent details of the crystal data and intensity collection are listed in Table 20. Otherwise, the data collection proceeded as described in Chapter II.

STRUCTURE SOLUTION AND REFINEMENT

The Patterson map was consistent with both space groups P1 and $P\bar{1}$, with one iridium atom per cell, since there were no Ir-Ir vectors apart from the origin peak. In the space group $P\bar{1}$ with Z = 1, the iridium atom is fixed at an inversion centre, and the molecule has crystallographically imposed inversion symmetry. For the space group P1, the position of the iridium atom can be arbitrarily fixed. The iridium atom was therefore placed at the origin (0,0,0) to be consistent with both space group possibilities. The electron density difference map phased on the iridium position, when carefully inspected, showed two triphenylphosphine groups which were not inversion related, and superimposed upon these were the inversion related images. This confirmed that the space group was the non-centrosymmetric choice P1. After fixing the positions of the two pseudo-trans PPh_3 groups, all subsequent atom positions were chosen such that they were consistent with this solution. In most instances the choice between the real atom position

Table 20. Summary of Data and Intensity Collection for $[IrCl((C_6H_4)COCC(C_6H_5)OPPh_2)(PPh_3)_2]\cdot C_6H_5CH_3$.

Compound	$[IrCl(C_6H_4COCC(C_6H_5)OP(C_6H_5)_2)-(P(C_6H_5)_3)_2]\cdot C_6H_5CH_3$
Formula	$C_{70}H_{57}O_2P_3Cl_1Ir_1$
Formula Weight	1250.81
Cell Parameters	
a	12.1972(8) Å
b	10.1629(10) Å
c	11.7608(12) Å
α	103.609(7)
β	95.059(7)°
γ	96.619(7)°
V	1397.4 Å^3
Z	1
Density	1.486 g·cm^{-3} (calcd.) 1.47(1) g·cm^{-3} (exptl. by floatation)
Space Group	$C_1^1 - P_1$
Crystal Dimensions	0.375 x 0.135 x 0.259 mm
Crystal Volume	0.0106 mm^3
Crystal Faces (and Distances from an arbitrary origin within the crystal (mm))	0 0 $\bar{1}$ 0.135 0 0 1 0.115 $\bar{1}$ 0 0 0.185 1 0 0 0.185 0 $\bar{1}$ 0 0.065 0 1 0 0.065 0 1 $\bar{1}$ 0.110 $\bar{1}$ 0 1 0.120
Temperature	20°C
Radiation	Cu Kα (λ = 1.540562 Å)
μ	61.672 cm^{-1}
Range in Absorption Correction Factors	0.256 - 0.499
Receiving Aperture	4mm x 4mm; 30 cm from the crystal

Table 20, continued

Takeoff Angle	3.5°
Scan Speed	2° in 2θ/min
Scan Range	0.90° below $K\alpha_1$ to 0.90° above $K\alpha_2$
Background Counting Time	10 s ($3° \leq 2\theta \leq 102°$); 20 s ($102° \leq 2\theta \leq 120°$)
2θ Limits	3.0 - 120.0°
2θ Limits for Centered Reflections	$45° \leq 2\theta \leq 65°$
Final Number of Variables	266
Unique Data Collected	4393
Unique Data Used ($F_o^2 \geq 3\sigma(F_o^2)$)	4387
Error in Observation of Unit Weight	1.378
R	0.028
R_w	0.038

and the inversion related image was unambiguous, since only the real position resulted in reasonable non-bonded contacts. In the final electron density difference maps, all hydrogen atoms except those of the toluene methyl group were unambiguously located.

Anomalous dispersion terms[18] for Ir, P and Cl were included in F_c. Full matrix least-squares refinement techniques were used, with atomic scattering factors from Cromer and Waber[19] for all atoms except hydrogen, for which the values from Stewart, Davidson and Simpson[20] were used. All phenyl carbons except those of the orthometallated ring were refined as rigid groups having D_{6h} symmetry and C-C distances of 1.392 Å. The non-group, non-hydrogen atoms were refined as individual anisotropic atoms, with the exception of the toluene methyl carbon atom, which was refined as an isotropic atom. All hydrogens, except for the methyl hydrogens of the toluene molecule, were included as fixed contributions and were not refined. Absorption corrections were applied as noted in Table 20.

Since the space group P1 is polar and the iridium atom has a large anomalous dispersion with Cu Kα radiation, the correct enantiomer must be determined to avoid polar dispersion errors, which would result in significant shifts in the positions of the Ir, P and Cl atoms relative to the lighter atoms and to each other.[21] A least squares refinement of the first model after location of all non-

hydrogen atoms converged to crystallographic residuals of $R = 0.067$ and $R_w = 0.097$, whereas the enantiomeric solution converged to $R = 0.045$ and $R_w = 0.061$. Since the latter model was significantly better than the initial one, it was assumed to be the correct enantiomer, and this model was used in all subsequent calculations. In agreement with this choice, the correct enantiomer showed a much narrower range in chemically equivalent Ir-P and P-C distances for the two triphenylphosphine groups (2.382(2) - 2.382(3)Å and 1.835(6) - 1.861(6)Å, respectively) than was observed for the other enantiomer (2.333(3) - 2.428(3)Å and 1.833(6) - 1.873(6)Å, respectively).

In the final electron density difference map, the top twenty residuals (0.77-0.38 e/Å^3) were located around the toluene of solvation, the iridium atom and the phenyl rings within the molecule. In earlier difference maps, a typical carbon atom had an electron density of *ca.* 3.3 e/Å^3. A more detailed discussion of the methods used in the structure solution and refinement is outlined in Chapter II.

RESULTS

A stereoview of the unit cell is shown in Figure 11. Four adjacent molecules are drawn in order to show some of the packing interactions. The crystallographic *a* axis runs from left to right, the *b* axis is from the top of the page to the bottom, and the *c* axis goes into the page.

Figure 12 presents the numbering scheme used within the molecule; the carbon atoms within the phosphorus phenyl rings are numbered with 3 digits, the first represents the phosphorus atom number, the second indicates the ring number, and the third digit represents the carbon atom within the ring; the phenyl hydrogens have the same numbering scheme as their attached carbon atom. The equatorial plane, which includes the ligand of interest, is shown in Figure 13 along with some relevant bond lengths and angles. The final positional and thermal parameters for the non-group and group atoms are presented in Tables 21 and 22, respectively. The idealized positional and thermal parameters for the hydrogen atoms are given in Table 23. Least squares plane calculations are presented in Table 24, while selected interatomic distances and bond angles are given in Tables 25 and 26, respectively. A listing of observed and calculated structure amplitudes is available.[22]

Figure 11. Cell Packing Diagram of $[IrCl(Ph_2POC(C_6H_5)-CCO(C_6H_4))(PPh_3)_2]\cdot C_6H_5CH_3$.

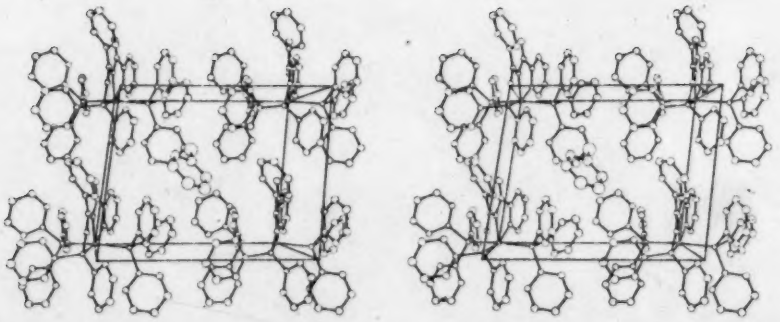


Figure 12. Perspective View of the [IrCl($Ph_2POC(C_6H_5)CCO-(C_6H_4)$)($PPh_3$)$_2$] Molecule.

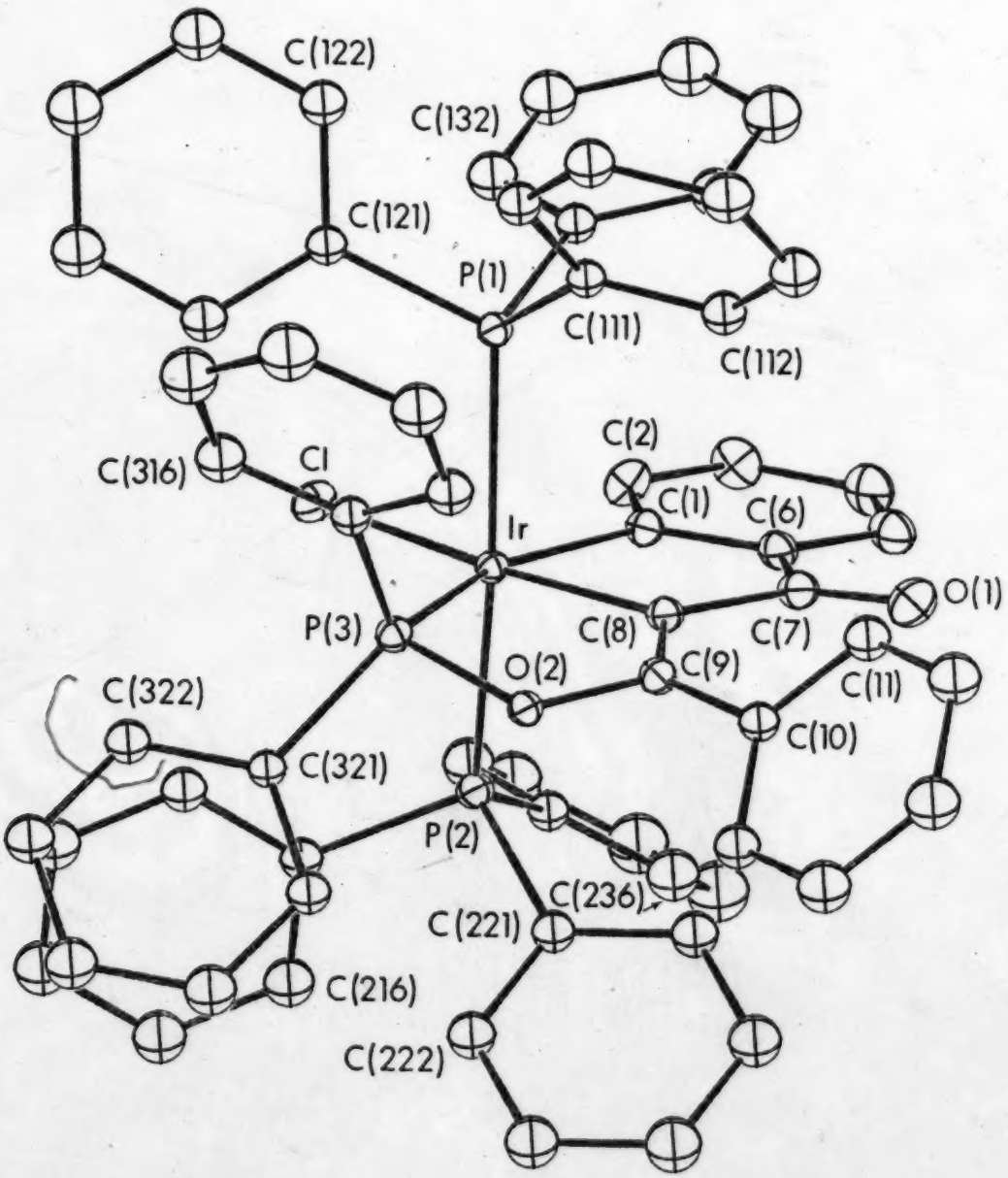


Figure 13. The Equatorial Plane of [IrCl($Ph_2POC(C_6H_5)$-$CCO(C_6H_4)$)$(PPh_3)_2$].

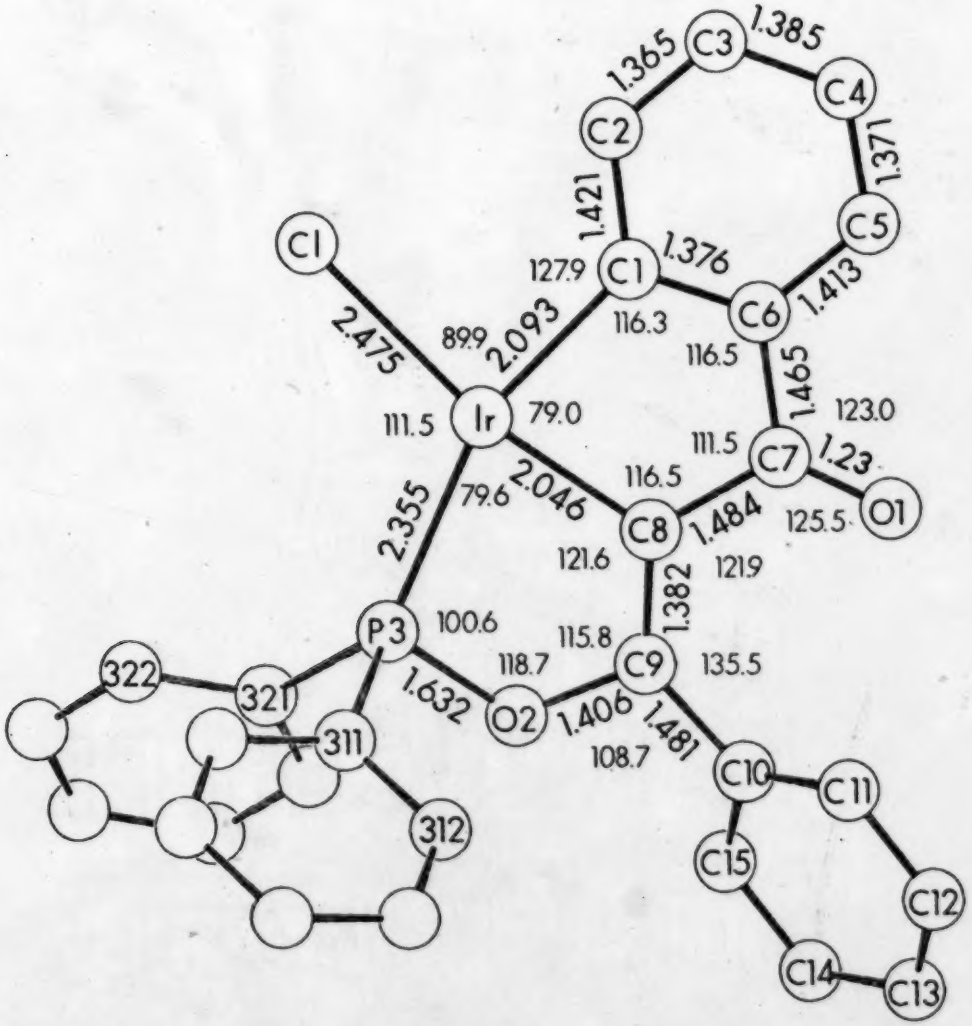


Table 21. Positional and Thermal Parameters For the Nongroup Atoms of [IrCl((C6H4)COCC(Ph)OPPH2)(PPh3)2].

Atom	x[a]	y	z	U11[b]	U22	U33	U12	U13	U23
Ir	0	0	0	2.57(1)	2.34(1)	2.76(1)	0.396(8)	0.300(9)	0.534(9)
P(1)	-0.1780(2)	0.0017(3)	0.0689(2)	2.8(1)	2.9(1)	3.0(1)	0.49(8)	0.43(9)	0.64(9)
P(2)	0.1903(2)	0.0211(3)	-0.0328(2)	2.9(1)	3.2(1)	3.6(1)	0.48(8)	0.5(1)	0.6(1)
P(3)	-0.0594(2)	0.0471(2)	-0.1804(2)	3.3(1)	2.67(10)	3.2(1)	0.46(8)	0.41(9)	0.73(9)
Cl	0.0536(2)	0.2124(2)	0.1584(2)	4.4(1)	3.4(1)	4.1(1)	0.08(8)	0.0(1)	-0.4(1)
C(8)	-0.0343(7)	-0.1940(9)	-0.1064(8)	3.2(4)	2.9(4)	3.6(5)	0.8(3)	0.8(4)	1.2(4)
O(2)	-0.0563(5)	-0.1006(5)	-0.2714(4)	5.6(3)	2.4(2)	3.0(2)	0.6(2)	0.4(2)	0.8(2)
C(9)	-0.0599(7)	-0.2177(8)	-0.2269(8)	3.9(4)	3.0(4)	3.3(4)	0.5(3)	0.6(4)	0.7(3)
O(1)	-0.0456(7)	-0.4293(5)	-0.0957(5)	10.0(5)	2.4(3)	5.6(3)	1.1(3)	0.4(3)	1.0(2)
C(7)	-0.0207(6)	-0.3070(8)	-0.0484(7)	3.8(4)	3.8(4)	4.2(4)	1.3(3)	1.1(3)	1.6(3)
C(6)	0.0281(6)	-0.2549(8)	0.0747(7)	3.7(4)	3.7(4)	4.2(4)	1.0(3)	1.0(3)	1.9(3)
C(1)	0.0414(6)	-0.1154(9)	0.1191(7)	3.2(4)	3.8(4)	3.4(4)	1.1(3)	0.5(3)	1.1(3)
C(2)	0.0838(8)	-0.067(1)	0.2402(8)	6.0(6)	5.4(5)	2.9(4)	0.8(4)	-0.5(4)	0.4(4)
C(3)	0.1103(8)	-0.154(1)	0.3082(7)	6.3(6)	7.0(6)	3.6(4)	1.0(5)	-0.7(4)	2.1(4)
C(4)	0.0975(8)	-0.293(1)	0.2596(8)	6.4(6)	6.7(6)	5.3(5)	1.8(5)	0.6(4)	3.3(4)
C(5)	0.0552(8)	-0.3459(9)	0.1436(8)	5.4(5)	4.6(5)	6.3(5)	1.3(4)	0.8(4)	2.8(4)
C(27)	-0.576(2)	-0.640(3)	-0.418(2)	10.1(5)[c]					

[a] Estimated standard deviations in the least signicant figure(s) are given in parentheses in this and all subsequent tables.

[b] The form of the thermal ellipsoid is: exp[-2*PI'(a*'U11h'+b*'U22k'+c*'U33l'+2a*b*U12hk+2a*c*U13hl+2b*c*U23kl)]. The quantities given in the table are the thermal coefficients x 10^2.

[c] Isotropic B(A').

Table 22. Derived Parameters For the Rigid Group Atoms of [IrCl((C6H4)COCC(Ph)OPPh2)(PPh3)2]·C6H5CH3.

Atom	x	y	z	B(A²)	Atom	x	y	z	B(A²)
C(21)	-0.575(1)	-0.563(1)	-0.507(1)	8.0(3)	C(121)	-0.2314(5)	0.1677(4)	0.1008(5)	3.0(1)
C(22)	-0.4926(9)	-0.459(1)	-0.5136(8)	9.7(5)	C(122)	-0.3250(5)	0.1785(4)	0.1602(5)	3.8(1)
C(23)	-0.504(1)	-0.391(1)	-0.603(1)	11.3(6)	C(123)	-0.3667(4)	0.3026(5)	0.1879(4)	4.9(2)
C(24)	-0.599(1)	-0.426(1)	-0.685(1)	12.2(7)	C(124)	-0.3148(5)	0.4157(4)	0.1563(5)	5.5(2)
C(25)	-0.6813(9)	-0.529(1)	-0.6785(8)	8.6(4)	C(125)	-0.2212(5)	0.4049(4)	0.0969(5)	5.0(2)
C(26)	-0.670(1)	-0.598(1)	-0.590(1)	6.8(3)	C(126)	-0.1795(4)	0.2809(5)	0.0691(4)	3.8(2)
C(10)	-0.0890(5)	-0.3404(5)	-0.3266(6)	3.0(1)	C(131)	-0.1818(7)	-0.0419(6)	0.2115(4)	3.0(1)
C(11)	-0.1678(5)	-0.4483(6)	-0.3207(4)	3.8(1)	C(132)	-0.1536(6)	0.0641(5)	0.3129(5)	4.4(2)
C(12)	-0.2007(5)	-0.5572(5)	-0.4190(5)	5.0(2)	C(133)	-0.1525(6)	0.0363(5)	0.4234(5)	5.5(2)
C(13)	-0.1547(5)	-0.5582(5)	-0.5234(6)	5.3(2)	C(134)	-0.1795(7)	-0.0974(6)	0.4324(4)	6.4(2)
C(14)	-0.0758(5)	-0.4503(6)	-0.5293(4)	5.1(2)	C(135)	-0.2077(6)	-0.2033(5)	0.3311(5)	6.0(2)
C(15)	-0.0430(5)	-0.3414(5)	-0.4310(5)	3.7(1)	C(136)	-0.2088(6)	-0.1756(5)	0.2206(5)	4.3(2)
C(311)	-0.2042(4)	0.0674(6)	-0.2281(4)	2.9(1)	C(211)	0.2591(4)	0.1920(4)	-0.0336(5)	3.2(1)
C(312)	-0.2755(5)	-0.0476(5)	-0.2934(6)	3.9(2)	C(212)	0.1995(3)	0.3014(6)	-0.0300(3)	3.7(1)
C(313)	-0.3827(4)	-0.0348(5)	-0.3364(5)	5.4(2)	C(213)	0.2541(4)	0.4291(5)	-0.0312(5)	5.0(2)
C(314)	-0.4187(4)	0.0929(6)	-0.3142(4)	6.3(2)	C(214)	0.3683(4)	0.4473(4)	-0.0360(5)	5.4(2)
C(315)	-0.3473(5)	0.2079(5)	-0.2489(6)	6.0(2)	C(215)	0.4279(3)	0.3378(6)	-0.0396(3)	5.1(2)
C(316)	-0.2401(4)	0.1951(5)	-0.2058(5)	4.4(2)	C(216)	0.3733(4)	0.2102(5)	-0.0384(5)	4.4(2)
C(321)	0.0134(5)	0.1535(5)	-0.2642(3)	2.6(1)	C(221)	0.2226(6)	-0.0858(5)	-0.1744(4)	3.3(1)
C(322)	0.0132(5)	0.2944(5)	-0.2335(4)	3.6(1)	C(222)	0.2642(6)	-0.0249(4)	-0.2590(5)	4.1(2)
C(323)	0.0601(5)	0.3749(4)	-0.3023(5)	4.3(2)	C(223)	0.2908(6)	-0.1057(5)	-0.3631(3)	5.1(2)
C(324)	0.1072(5)	0.3146(5)	-0.4019(3)	4.9(2)	C(224)	0.2758(6)	-0.2475(5)	-0.3826(4)	5.6(2)
C(325)	0.1073(5)	0.1737(5)	-0.4326(4)	4.8(2)	C(225)	0.2341(6)	-0.3084(4)	-0.2980(5)	5.0(2)
C(326)	0.0604(5)	0.0932(4)	-0.3637(5)	3.4(1)	C(226)	0.2075(6)	-0.2276(5)	-0.1939(3)	4.0(2)
C(111)	-0.2958(4)	-0.1162(5)	-0.0261(4)	2.7(1)	C(231)	0.2876(5)	-0.0156(7)	0.0821(4)	3.1(1)
C(112)	-0.2893(4)	-0.2557(5)	-0.0582(3)	3.5(1)	C(232)	0.3164(6)	0.0877(5)	0.1851(6)	4.7(2)
C(113)	-0.3781(4)	-0.3459(4)	-0.1272(5)	4.5(2)	C(233)	0.3928(6)	0.0711(6)	0.2740(6)	5.6(2)
C(114)	-0.4733(4)	-0.2966(5)	-0.1641(4)	4.8(2)	C(234)	0.4405(5)	-0.0489(7)	0.2598(4)	6.7(3)
C(115)	-0.4798(4)	-0.1571(5)	-0.1320(3)	4.4(2)	C(235)	0.4117(6)	-0.1523(5)	0.1567(6)	6.9(3)
C(116)	-0.3910(4)	-0.0669(4)	-0.0630(5)	3.5(1)	C(236)	0.3353(6)	-0.1357(6)	0.0679(6)	5.0(2)

Table 22, continued

Rigid Group Parameters

	Xc[a]	Yc	Zc	Delta[b]	Epsilon	Eta
Ring1	-0.5870(7)	-0.4944(8)	-0.5961(7)	3.982(8)	2.39(1)	2.30(1)
Ring2	-0.1218(3)	-0.4493(4)	-0.4250(3)	0.624(4)	1.115(5)	2.016(4)
Ring3	-0.3114(3)	0.0802(4)	-0.2711(3)	-0.105(4)	2.802(4)	3.367(3)
Ring4	0.0603(3)	0.2341(4)	-0.3330(3)	3.149(4)	1.083(4)	2.602(3)
Ring5	-0.3846(3)	-0.2064(4)	-0.0951(3)	-0.056(4)	2.738(3)	2.581(3)
Ring6	-0.2731(3)	0.2917(4)	0.1285(3)	2.959(4)	0.638(4)	1.243(3)
Ring7	-0.1806(4)	-0.0696(4)	0.3220(4)	0.271(4)	1.637(4)	0.207(3)
Ring8	0.3137(3)	0.3196(4)	-0.0348(3)	2.917(4)	0.163(4)	2.106(3)
Ring9	0.2492(3)	-0.1667(4)	-0.2785(3)	3.232(4)	1.208(4)	3.796(3)
Ring10	0.3640(4)	-0.0323(5)	0.1709(4)	-0.310(4)	2.243(5)	0.224(4)

[a] Xc,Yc and Zc are the fractional coordinates of the centroid of the rigid group.

[b] The rigid group orientation angles Delta,Epsilon and Eta(radians) are the angles by which the rigid body is rotated with respect to a set of axes X,Y and Z. The origin is the centre of the ring; X is parallel to a* , Z is parallel to c and Y is parallel to the line defined by the intersection of the plane containing a* and b* with the plane containing b and c.

Table 23. Idealized Positional and Thermal Parameters For the Hydrogen Atoms of [IrCl((C6H4)COCC(Ph)OPPh2)(PPh3)2]·C6H5CH3.

Atom	x	y	z	B(A²)	Atom	x	y	z	B(A²)
H(2)	0.0936	0.0279	0.2752	4.95	H(125)	-0.1857	0.4822	0.0751	5.98
H(3)	0.1381	-0.1170	0.3891	5.37	H(126)	-0.1156	0.2735	0.0284	4.80
H(4)	0.1175	-0.3531	0.3068	5.52	H(132)	-0.1350	0.1553	0.3066	5.38
H(5)	0.0444	-0.4420	0.1101	5.06	H(133)	-0.1329	0.1088	0.4925	6.49
H(11)	-0.1991	-0.4475	-0.2495	4.76	H(133)	-0.1785	-0.1161	0.5079	7.40
H(12)	-0.2543	-0.6308	-0.4150	5.99	H(135)	-0.2261	-0.2944	0.3374	6.94
H(13)	-0.1769	-0.6324	-0.5905	6.29	H(136)	-0.2282	-0.2479	0.1515	5.35
H(14)	-0.0443	-0.4508	-0.6006	6.13	H(212)	0.1217	0.2892	-0.0269	4.69
H(15)	0.0109	-0.2675	-0.4351	4.67	H(213)	0.2135	0.5039	-0.0290	6.02
H(312)	-0.2509	-0.1349	-0.3084	4.94	H(214)	0.4057	0.5345	-0.0371	6.42
H(313)	-0.4313	-0.1136	-0.3810	6.37	H(215)	0.5060	0.3503	-0.0431	6.18
H(314)	-0.4918	0.1013	-0.3439	7.29	H(216)	0.4141	0.1356	-0.0410	5.40
H(315)	-0.3719	0.2949	-0.2343	6.95	H(222)	0.2746	0.0716	-0.2457	5.09
H(316)	-0.1914	0.2736	-0.1617	5.41	H(223)	0.3193	-0.0645	-0.4208	6.10
H(322)	-0.0189	0.3357	-0.1656	4.59	H(224)	0.2938	-0.3030	-0.4536	6.64
H(323)	0.0601	0.4711	-0.2814	5.36	H(225)	0.2236	-0.4053	-0.3113	6.00
H(324)	0.1392	0.3695	-0.4489	5.90	H(226)	0.1789	-0.2692	-0.1361	4.96
H(325)	0.1393	0.1325	-0.5006	5.86	H(232)	0.2838	0.1695	0.1950	5.71
H(326)	0.0603	-0.0030	-0.3848	4.42	H(233)	0.4125	0.1417	0.3445	6.61
H(112)	-0.2243	-0.2894	-0.0330	4.52	H(234)	0.4928	-0.0601	0.3207	7.66
H(113)	-0.3737	-0.4411	-0.1491	5.48	H(235)	0.4444	-0.2341	0.1473	7.82
H(114)	-0.5340	-0.3581	-0.2111	5.83	H(236)	0.3157	-0.2063	-0.0023	5.98
H(115)	-0.5449	-0.1234	-0.1570	5.42	H(22)	-0.4285	-0.4392	-0.4541	11.66
H(116)	-0.3955	0.0283	-0.0409	4.50	H(23)	-0.4449	-0.3211	-0.6021	12.63
H(122)	-0.3603	0.1014	0.1819	4.83	H(24)	-0.6022	-0.3770	-0.7427	14.21
H(123)	-0.4304	0.3101	0.2286	5.86	H(25)	-0.7430	-0.5511	-0.7354	9.86
H(124)	-0.3432	0.5005	0.1752	6.54	H(26)	-0.7266	-0.6692	-0.5875	8.31

Table 24. Least Squares Plane Calculations.[a]

plane no.	equation
1	-0.1670X + 0.9519Y - 0.2568Z - 0.000 = 0
2	0.9523X + 0.1483Y - 0.2667Z - 0.000 = 0
3	0.9672X + 0.1428Y - 0.2102Z - 0.000 = 0
4	0.9576X + 0.1401Y - 0.2518Z + 0.0625 = 0
5	0.9636X + 0.1062Y - 0.2453Z - 0.0120 = 0
6	0.9844X + 0.1281Y - 0.1203Z + 0.0814 = 0

Deviations from the Planes (Å)

	Plane no.					
Atom	1	2	3	4	5	6
Ir	0.00	0.00	0.00		-0.012	0.084
P(1)	0.00					
P(2)	0.00					
P(3)			0.00			-0.125(2)
Cl		0.00			-0.042(3)[b]	0.321(3)[b]
C(8)		0.00			0.031(9)	-0.062(9)
O(2)						0.143(6)
C(9)						-0.040(8)
O(1)					-0.131(8)[b]	
C(7)				-0.063(8)[b]	-0.039(8)	
C(6)				-0.002(8)	0.027(8)	
C(1)			0.00	0.005(8)	-0.006(8)	
C(2)				-0.001(10)		
C(3)				-0.007(10)		
C(4)				0.010(10)		
C(5)				-0.005(9)		

Dihedral Angles Between Planes

Plane A	Plane B	angle(deg)
1	2	87.1
1	3	88.4
1	4	87.8
1	5	89.8
1	6	90.7
2	3	3.4
2	4	1.0
2	5	2.8
2	6	8.7
3	4	2.5
3	5	2.9
3	6	5.3
4	5	2.01
4	6	7.7
5	6	7.4

[a]X, Y and Z are the orthogonal coordinates (Å) with X along the a axis, Y in the (a-b) plane and Z along the c^* axis.

[b]Not included in the least squares plane calculation.

Table 25. Selected Interatomic Distances (Å) in $[IrCl(C_6H_4COCC(C_6H_5)OPPh_2)(PPh_3)_2]\cdot C_6H_5CH_3$.

BONDED CONTACTS

Ir-P(1)	2.384(3)	O(2)-C(9)	1.406(9)
Ir-P(2)	2.380(3)	C(9)-C(10)	1.481(9)
Ir-P(3)	2.355(2)	C(9)-C(8)	1.382(12)
Ir-Cl	2.475(2)	C(8)-C(7)	1.484(11)
Ir-C(1)	2.093(7)	C(7)-O(1)	1.227(10)
Ir-C(8)	2.046(9)	C(7)-O(1)*	1.260(10)
P(1)-C(111)	1.854(4)	C(7)-C(6)	1.465(11)
P(1)-C(121)	1.846(5)	C(6)-C(1)	1.376(12)
P(1)-C(131)	1.836(5)	C(1)-C(2)	1.421(12)
P(2)-C(211)	1.842(5)	C(2)-C(3)	1.365(14)
P(2)-C(221)	1.864(5)	C(3)-C(4)	1.385(14)
P(2)-C(231)	1.852(5)	C(4)-C(5)	1.371(14)
P(3)-C(311)	1.854(5)	C(5)-C(6)	1.413(11)
P(3)-C(321)	1.834(4)	C(21)-C(27)	1.44 (3)
P(3)-O(2)	1.632(5)		

NON-BONDED CONTACTS

Cl-H(2)	2.636(3)	C(27)-H(233)[b]	3.11(3)
Cl-H(212)	2.648(3)	C(312)-H(133)[c]	2.694(6)
Cl-H(126)	2.677(3)	O(2)-C(321)	2.603(6)
Cl-C(126)	3.153(6)	C(322)-H(212)	2.677(5)
Cl-C(212)	3.188(6)	C(126)-H(316)	2.688(5)
Cl-C(1)	3.238(9)	H(316)-H(322)	2.13
O(2)-H(326)	2.328(5)	H(323)-H(225)[d]	2.33
O(2)-H(312)	2.345(6)	H(112)-H(136)	2.12
C(9)-H(312)	2.737(8)	H(126)-H(316)	2.34
O(1)-H(322)[a]	2.406(6)	H(13)-H(132)[e]	2.35
C(7)-H(112)	2.530(7)	H(226)-H(236)	2.12
C(7)-H(226)	2.748(7)	H(235)-H(24)[f]	2.22

*corrected for riding motion where the second atom is riding on the first.

[a]Atom is positioned at x, -1+y, z.

[b]Atom is positioned at -1+x, -1+y, -1+z.

[c]Atom is positioned at x, y, -1+z.

[d]Atom is positioned at x, 1+y, z.

[e]Atom is positioned at x, 1+y, 1+z.

[f]Atom is positioned at 1+x, y, 1+z.

Table 26. Selected Bond Angles (deg) in [IrCl(C_6H_4-COCC(C_6H_5)OPPh$_2$)(PPh_3)$_2$]·$C_6H_5CH_3$.

P(1)-Ir-P(2)	169.46(8)	C(321)-P(3)-O(2)	97.2(2)
P(1)-Ir-P(3)	94.64(7)	P(3)-O(2)-C(9)	118.7(5)
P(1)-Ir-Cl	84.58(8)	O(2)-C(9)-C(8)	115.8(7)
P(1)-Ir-C(1)	88.1(2)	O(2)-C(9)-C(10)	108.7(6)
P(1)-Ir-C(8)	95.4(2)	C(10)-C(9)-C(8)	135.5(7)
P(2)-Ir-P(3)	93.18(8)	C(9)-C(8)-C(7)	121.9(8)
P(2)-Ir-Cl	85.98(9)	C(8)-C(7)-O(1)	125.5(8)
P(2)-Ir-C(1)	87.3(2)	C(8)-C(7)-C(6)	111.5(7)
P(2)-Ir-C(8)	92.9(3)	O(1)-C(7)-C(6)	123.0(7)
P(3)-Ir-Cl	111.54(8)	C(7)-C(6)-C(1)	116.5(6)
P(3)-Ir-C(1)	158.5(2)	C(7)-C(6)-C(5)	120.6(7)
P(3)-Ir-C(8)	79.6(2)	C(6)-C(1)-C(2)	115.7(7)
Cl-Ir-C(1)	89.9(3)	C(1)-C(2)-C(3)	122.3(8)
Cl-Ir-C(8)	168.9(2)	C(2)-C(3)-C(4)	120.2(8)
C(1)-Ir-C(8)	79.0(4)	C(3)-C(4)-C(5)	120.1(7)
Ir-P(1)-C(111)	117.2(2)	C(4)-C(5)-C(6)	118.8(8)
Ir-P(1)-C(121)	116.5(2)	C(5)-C(6)-C(1)	122.8(8)
Ir-P(1)-C(131)	113.5(2)	P(1)-C(111)-C(112)	119.3(3)
Ir-P(2)-C(211)	117.6(2)	P(1)-C(111)-C(116)	120.7(3)
Ir-P(2)-C(221)	116.0(2)	P(1)-C(121)-C(122)	118.2(3)
Ir-P(2)-C(231)	115.4(2)	P(1)-C(121)-C(126)	121.8(3)
Ir-P(3)-C(311)	124.6(2)	P(1)-C(131)-C(132)	117.6(3)
Ir-P(3)-C(321)	129.7(2)	P(1)-C(131)-C(136)	122.4(3)
Ir-P(3)-O(2)	100.6(2)	P(2)-C(211)-C(212)	121.5(3)
Ir-C(8)-C(9)	121.6(6)	P(2)-C(211)-C(216)	118.5(3)
Ir-C(8)-C(7)	116.3(6)	P(2)-C(221)-C(222)	120.5(3)
Ir-C(1)-C(6)	116.3(6)	P(2)-C(221)-C(226)	119.5(3)
Ir-C(1)-C(2)	127.9(7)	P(2)-C(231)-C(232)	116.2(3)
C(111)-P(1)-C(121)	103.2(3)	P(2)-C(231)-C(236)	123.8(4)
C(111)-P(1)-C(131)	103.4(3)	P(3)-C(311)-C(312)	118.4(3)
C(121)-P(1)-C(131)	100.9(3)	P(3)-C(311)-C(316)	121.5(3)
C(211)-P(2)-C(221)	102.0(3)	P(3)-C(321)-C(322)	119.5(3)
C(211)-P(2)-C(231)	98.7(3)	P(3)-C(321)-C(326)	120.3(3)
C(221)-P(2)-C(231)	104.8(3)	C(22)-C(21)-C(27)	126 (1)
C(311)-P(3)-C(321)	98.7(2)	C(26)-C(21)-C(27)	114 (1)
C(311)-P(3)-O(2)	97.5(3)		

DESCRIPTION OF STRUCTURE

The unit cell of 2 consists of a discrete iridium monomer and one molecule of toluene of solvation. There are two non-bonded contacts between these two molecules, which are somewhat less than the sum of their van der Waals radii.[23] These contacts are between the toluene methyl group (C27) and a triphenylphosphine hydrogen atom (H(233), 3.11(3)Å) and between a hydrogen of the toluene phenyl ring (H(24)) and another triphenylphosphine hydrogen atom (H(235), 2.22 Å). The carbon atoms within the toluene molecule (C21 - C27) have large thermal parameters, which is not unusual for such molecules of solvation.[24] The bond length between the phenyl ring and the methyl group (C(21)-C(27), 1.44(3)Å) is somewhat shorter than in other reported structures with a toluene of solvation, but this is probably a consequence of the poor description of this molecule as shown by the large thermal motion of this group.

Within the iridium monomer, the coordination about the metal centre is quasi-octahedral. Two triphenylphosphine groups, which are mutually trans occupy the axial positions while a chlorine atom and the unusual tridentate ligand, $((C_6H_4)COCC(C_6H_5)OPPh_2)$, occupy the equatorial sites, with the tridentate ligand coordinating through an orthometallated phenyl ring, a metallated vinylic carbon atom and a phosphorus atom. The chlorine atom is trans to the olefinic

carbon atom (C(8)), while the metallated phenyl ring (C(1)-C(6)) and the diphenylphosphine group (P(3)), are mutually trans. Coordination about the iridium atom is distorted slightly from an octahedral geometry as a result of the constraints imposed by the chelating ligand and the large bulk of the ligands. Consequently, the P(3)-Ir-C(1) angle (158.5(2)°), and the P(3)-Ir-C(8) and C(8)-Ir-C(1) angles (79.6(2)° and 79.0(4)°, respectively) are significantly different than the idealized values of 180° and 90°. Furthermore, the Cl-Ir-C(8) angle is 168.9(2)°, with the chlorine atom bent away from the Ph_2P group of the tridentate ligand (P(3)-Ir-Cl = 111.54(8)°). In the axial plane, the two triphenylphosphine groups (P(1) and P(2)) are bent back away from the C(1)-C(8)-P(3) plane, with a P(1)-Ir-P(2) angle of 169.46(8)°. This forces the PPh_3 groups closer to the chlorine atom (P(1)-Ir-Cl = 84.58(8)° and P(2)-Ir-Cl = 85.98(9)°), resulting in two close, non-bonded contacts between the hydrogens of the phenyl rings and the chlorine atom (Cl-H(212), 2.648(3)Å; Cl-H(126), 2.677(3)Å). There is also a close non-bonded contact between the chlorine atom and H(2) (2.636(3)Å) of the orthometallated ring of the ligand. These contacts are significantly shorter than normal Cl-H van der Waals contacts of 3.0 Å.[23] The two PPh_3 groups are bent away from the tridentate ligand in order to minimize the steric interactions between the phenyl rings and this bulky ligand. As it is, there are still two

short non-bonded contacts between C(7) of the ligand and two hydrogen atoms from the triphenylphosphine groups (C(7)-H(112), 2.530(7)Å; C(7)-H(226), 2.748(7)Å).

The two Ir-P bond distances for the mutually trans phosphine groups (P(1), 2.384(3); and P(2), 2.380(3)Å) agree very well with each other, and are typical for this type of bond.[25] The Ir-P-C bond angles (average 116.0(15)°), the C-P-C bond angles (average 102.2(20)°), and the P-C bond lengths (average 1.849(9)Å) are also as expected for triphenylphosphine groups.

The Ir-Cl bond length of 2.475(2)Å is considerably longer than that found in Ir(III) complexes in which two chlorine atoms are trans to each other where values of *ca.* 2.338(2)Å are typical,[26] and results from the large trans influence of the σ-bound olefinic carbon atom. Analogous lengthening of the Ir-Cl bond has been observed in other octahedral iridium III complexes where the chlorine atom is trans to an sp^2 hybridized carbon atom[27-31] resulting in Ir-Cl distances ranging from 2.44(1) to 2.52(2)Å.

The unusual tridentate ligand in the equatorial plane has resulted from the condensation of the carbene ligand, formed from the loss of N_2 from dibenzoyldiazomethane, and a diphenylphosphine group, such that the two groups are fused at a ketonic oxygen and the phosphorus atom. This tridentate ligand is bound to the metal through the phosphorus atom and is also bimetallated at the vinylic posi-

tion of C(8) and at the orthocarbon atom, C(1), of one of the benzoyl groups, such that the resulting chelate consists of two five-membered rings adjacent to each other (see Figure 13). This iridium complex is not unlike the two Rh complexes $[RhCl((C_6H_5)CONCS)_2(PPh_3)_2]$[32] and $[RhCl(EtOCONCS)_3(PPh_3)_2]$[33] which contain tridentate ligands formed from the condensation of isothiocyanate molecules. The two five-membered metallocycle rings in the present complex are planar to within 0.14 Å (Ir-P(3)-O(2)-C(9)-C(8)) and 0.04 Å (Ir-C(8)-C(7)-C(6)-C(1)), and are inclined to each other by 7.4°, indicating that the whole ligand is essentially planar. This was also seen for the two Rh complexes, mentioned above.[32,33] The chlorine atom is displaced 0.32 Å from the plane of the first chelated ring, and 0.04 Å from the second. The second chalate ring, Ir-C(8)-C(7)-C(6)-C(1) is virtually planar with the orthometallated ring (C(1)-C(6)), with an angle between the two planes of 2.0°. The oxygen atom is out of the plane of the second chelate ring by 0.14 Å.

Within the first 5-membered ring (P(3)-O(2)-C(9)-C(8)-Ir), the Ir-P(3) bond length (2.355(2)Å) is significantly shorter than those of the two mutually trans triphenylphosphine groups (average 2.382(2)Å). This difference may reflect the difference between the phosphine groups, since the former group now contains a phosphite linkage, or may result from chelate strain, forcing the diphenylphosphine

linkage closer to the metal. The strain of the chelate linkage is evident in the coordination about P(3), which is significantly distorted from a tetrahedral geometry. Therefore the Ir-P(3)-O(2) bond angle (100.6(2)°) is small, and the Ir-P(3)-C(311) and Ir-P(3)-C(321) bond angles (124.6(2) and 129.7(6)°, respectively) are larger than in the PPh_3 groups (average 116.0(15)°). Within the PPh_2 moiety, the P(3)-C bond lengths are normal and comparable to those of the PPh_3 groups. The phosphorus-oxygen bond length, 1.632(5)Å indicates a P-O single bond and is comparable to the P-O bond lengths (ranging from 1.60(1) to 1.63(1)Å) found in the orthometallated phosphite complex $[(C_8H_{14})Ir(P(OC_6H_3Me)(OC_6H_4Me)_2)((POCH_2)_3CMe)]$, [34] with the P-O bond within the metallated phosphite group having a value of 1.61(1)Å.

Viewing the remainder of the tridentate ligand, *i.e.* that part which originated from the dibenzoyldiazomethane molecule, it is evident from the structural parameters that this group is bonded to the iridium atom as a metallated olefinic group and as an orthometallated phenyl ring. Therefore the C(8)-C(9) bond length (1.382(12)Å) is close to that of a normal C=C double bond (1.34 Å), [23] and is considerably shorter than the analogous distances (average 1.473(4)Å) in the starting diazoalkane molecule. In contrast to this, the C(7)-C(8) distance of 1.484(11)Å is typical of a C-C single bond between sp^2 hybridized carbon

atoms[23] and is comparable to the value observed in the uncomplexed diazoalkane molecule. The geometries about both C(8) and C(9) are trigonal planar, with the angles about C(8) deviating only slightly from the idealized trigonal geometry, whereas around C(9) the angles are somewhat more distorted with O(2)-C(9)-C(8), O(2)-C(9)-C(10) and C(8)-C(9)-C(10) angles of 115.8(7)°, 108.7(6)° and 135.5(7)°, respectively. This distortion, which widens the C(10)-C(9)-C(8) angle, results from the strain imposed by the Ir-P(3) distance, which is relatively long compared to the other distances within the metallocycle. Again, it is noted that this strain at C(9) opposes any further lengthening of the Ir-P(3) distance and may be responsible for this distance being shorter than the other Ir-P distances in the structure. In addition, this strain may be responsible for the deviations from planarity of this chelate ring, as O(2) is 0.143(6)Å above the plane and P(3) is 0.125(2)Å below the plane.

Also consistent with the olefinic formulation for the C(8)-C(9) bond, the C(9)-O(2) bond, 1.406(9)Å, is close to a normal C-O single bond (1.40 Å),[23] and the C(9)-C(10) distance (1.481(9)Å) indicates a normal C-C single bond.[23] The phenyl ring, C(10) through C(15), is skewed from the metallocycle ring by 72.5°, in order to minimize contacts with O(1) and the phenyl rings of the diphenylphosphine moiety.

Within the remainder of the tridentate ligand, the parameters are close to those in the free diazoketone (see Chapter III). Thus, C(7)-O(1) (1.227(10)Å) is close to the uncorrected values in dibenzoyldiazomethane (average 1.223(3)Å) and indicates a bond order of two.[35] In addition C(6)-C(7), at 1.465(11)Å, is not significantly different from the corresponding distances in the free diazoalkane molecule (average 1.488(2)Å). The distances within the orthometallated ring, C(1)-C(6), range from 1.365(14) to 1.421(12)Å and are not unusual for such a group. While the bonding parameters within the coordinated ligand are not significantly different from the uncomplexed diazoalkane molecule, the slight differences are consistent with a somewhat higher degree of delocalization within the coordinated ligand. This may result from the increased planarity of the diazoalkane molecule in the metal complex, especially between the orthometallated phenyl ring and the metallocycle ring, Ir-C(8)-C(7)-C(6)-C(1).

Both Ir-C(1) and Ir-C(8) distances (2.093(7) and 2.046(9)Å, respectively) are comparable with other Ir(III) complexes in which the metal is σ-bound to an sp^2-hybridized carbon atom (range 1.99(2)-2.16 Å).[27-31] The longer distance for the orthometallated Ir-C(1) bond in comparison to Ir-C(8) may result from the larger trans influence of P(3) compared to Cl, or it may reflect the restrictions put on C(8) by the rest of the tridentate ligand. In other tri-

dentate ligands where the central metal linkage has been a carbon atom, these metal carbon bonds have been unusually short.[32,33,36]

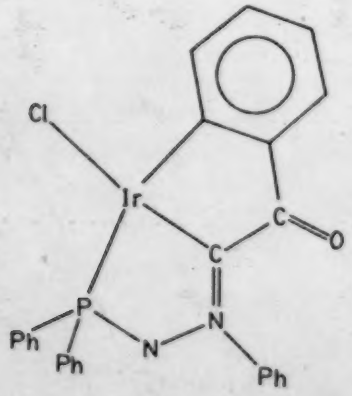
DISCUSSION

STRUCTURE OF $[IrCl((C_6H_4)COCC(C_6H_5)OPPh_2)(PPh_3)_2]\cdot C_6H_5CH_3$

Complex 2 is rather novel in that it contains the unusual tridentate ligand, $((C_6H_4)COCC(C_6H_5)OPPh_2)$ formed from a dibenzoyl carbene fragment and a PPh_2 group. This complex was formed in the reaction of $[IrCl(C_8H_{14})]_2$ with PPh_3 and $(PhCO)_2CN_2$, in which the diazoalkane ligand has lost N_2, coordinated to the metal centre through the carbene carbon atom, and has undergone orthometallation of one of the phenyl rings. In addition one of the ketonic oxygen atoms has coordinated to a PPh_2 group, which is coordinated to the metal via the phosphorus atom. The diphenylphosphine group bonded to the ketonic oxygen (O(2)), originated, presumably, from a triphenyl phosphine group, since only PPh_3 was used in the reaction mixture. Consequently, fragmentation of PPh_3 must have occurred, with the loss of a phenyl ring. Activation of P-C bonds have been reported for various metal complexes including those of Rh and Ir,[37,38] Ru[39] and Os.[40] In most cases bridging PR_2 groups result, with the third R group absent from the complex. For example, refluxing either $[Ir(CO)H(PPh_3)_3]$ or $[IrH_3(PPh_3)_3]$ in DMF or decalin results in the formation of $[Ir(CO)(PPh_3)\mu\text{-}(PPh_2)]_2$,[38]

presumably with the loss of benzene. However, in the complex, $[(\eta^5\text{-}C^5H_5)Ir\text{-}\mu\{C(Ph)O\}\text{-}\mu\text{-}\{C(CH_3)O\}\text{-}\mu\text{-}(PPh_2)Mn(CO)_3]$,[37] the phenyl group migrated to a carbonyl ligand. In the present complex, there is no evidence of the fragmented phenyl ring; nor is there evidence of the hydrido ligand resulting from the orthometallation reaction. The distorted octahedral coordination about the iridium atom shows no vacant coordination site in which the hydrido ligand could be located and no electron density consistent with such a ligand was observed. Furthermore, the complex, as it is formulated, is an 18 e^- compound and cannot accommodate the extra hydride ligand. We assume therefore that at some stage, metal activation of the P-phenyl bond has occurred with reductive elimination of the phenyl group and hydride ligand as benzene. The phenyl ring fragmentation may have resulted from increased steric interactions after coordination of the diazoalkane ligand to an intermediate such as $[IrCl(PPh_3)_3]$.

Another conceivable possibility for this complex would have a dinitrogen containing fragment as presented below.



Such a species (having the PPh_3 groups above and below the plane shown) could result from attack by the diazoalkane molecule at a coordinated PPh_3 group, cleavage of one benzoyl group, and migration of a phenyl group from the PPh_3 ligand to one of the nitrogen atoms. Certainly $Ph_3P\text{-}NNCR_2$ compounds resulting from the reactions of phosphines with diazoalkane molecules are well known (*vide infra*). In addition, migration of a phenyl group has been observed, as in the formation of $[Fe_2(CO)_6](\mu\text{-}PPh_2)(\mu\text{-}PPh\ C{=}C(CF_2)_2(CF_2)_2C{=}CPh)$ from the starting ditertiary phosphine $(Ph_2PC{=}C(CF_2)_2(CF_2)_2C{=}CPPh_2)$.[41] However the observed geometry in the present structure is not as consistent with this possibility, since the nitrogen atom bound to phosphorus would be significantly displaced from the ligand plane, having a P-N-N angle which would be close to the tetrahedral value. Furthermore, we would expect a shorter C=N bond than is observed. In order to crystallographically verify that the correct solution involved a carbonyl fragment (C(9)-O(2)), and not a dinitrogen fragment, the latter model was refined to convergence. The poorly behaved thermal parameters[42] and the poorer crystallographic residuals for the model involving nitrogen atoms ($R = 0.029$ $R_w = 0.038$), confirmed that a carbonyl fragment was involved, as shown in Figures 12 and 13.

Compound 2 can be considered as an Ir(III) complex, with the $((C_6H_4)COCC(Ph)OPPh_2)$ ligand formally a dianionic

ligand, and the metallated phenyl carbon (C(1)) and the metallated C(8) atom both negatively charged. This would indicate that C(8) is not a carbene atom (which is a neutral 2 electron donor), but an unsaturated carbon atom, similar to that found in metallated phenyl rings. Consistent with this, the bond between C(8)-C(9) is a double bond, rather than a single bond as expected for a carbene atom, and C(8) is best considered as a metallated olefinic carbon atom.

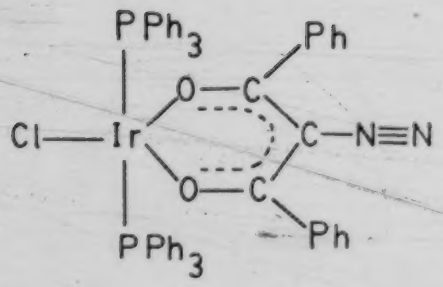
The original bonding parameters within the parent diazoalkane molecule have changed considerably upon coordination to the iridium complex. Overall, the ligand is considerably more planar than before complexation, which leads to a greater amount of electron delocalization. This is seen is the lengthened C(7)-O(1) bond and shortened C(7)-C(6) bond as compared to the free aliphatic diazo molecule. The other C-O group within the coordinated ligand is completely different from the free molecule, as the oxygen is bonded to both C(9) and P(3) rather than just one carbon atom. This in turn results in a C=C double bond between C(9)-C(8), as compared to the same bond in the free molecule, which had a bond order of *ca.* 1.5.

REACTION OF $[IrCl(N_2)(PPh_3)_2]$ AND $(PhCO)_2CN_2$

The free dibenzoyldiazomethane molecule has infrared stretching frequencies of 2100 cm^{-1} for ν_{NN} and 1625, 1596

and 1575 cm^{-1} for ν_{CO}, while $[IrCl(N_2)(PPh_3)_2]$ has an NN stretching frequency of 2105 cm^{-1}. [5] After reaction, the yellow crystalline compound (1) shows a single band above 1500, at 1954 cm^{-1}. Since the N_2 group of $[IrCl(N_2)(PPh_3)_2]$ is very labile, and is not expected to be retained during the reaction, this 1954 cm^{-1} band is assigned to ν_{NN} of the coordinated aliphatic diazo ligand. The mass spectral data of 1 support this conclusion, since the highest peak of 974 m/e (assigned to $[IrCl(PPh_3)_2(PhCOCCOPh)]^+$) and the peaks at 224 and 223 m/e ($PhCOCH_2COPh^+$ and $PhCOCHCOPh^+$, respectively) indicate that the ligand is indeed present. Although the diazoalkane N_2 group is not observed in the mass spectrum, this does not indicate that it is absent in (1) since the N_2 group cleavage is quite facile under the conditions used to obtain the mass spectrum. A similar N_2 cleavage was observed in the mass spectrum of the parent diazoalkane molecule. Other peaks in the mass spectrum were consistent with the assignment of the highest peak to an iridium complex (*i.e.* 938 $(Ir(PPh_3)_2(C(COPh)_2)^+)$; 780 $(IrCl(CO)(PPh_3)_2^+)$; 751 $(IrCl(PPh_3)_2^+)$; 716 $(Ir(PPh_3)_2^+)$ and 638 m/e $(Ir(PPh_3)(PPh_2))^+$).

The CO stretching bands are not in the expected area around 1600 cm^{-1}, indicating that coordination of the ligand to the metal has greatly altered the CO bonds. Compound 1 is most likely then, a five-coordinate iridium complex, with the diazoalkane ligand chelated through the oxygen atoms.



1

This would be an 18 e^- system, with trans phosphine ligands, consistent with the $^{31}P\{^1H\}$ NMR spectrum, which showed a singlet. This complex is analogous to metal-acetylacetone complexes in which the ν_{CO} bands occur below 1700 cm^{-1}. [43] In the infrared spectrum of 1, there were no bands below 1600 cm^{-1} which could be assigned to the CO group of the diazoalkane ligand. However, the chelated structure is the most consistent one, in view of all the data. Preliminary X-ray crystallographic work on crystals of 1 indicated twinning within the crystals, which were also of poor diffraction quality, and a structure determination was not attempted. An elemental analysis was not carried out since compound 1 was considered pure only if single crystals were obtained, and the yield of crystals of 1 from the reaction was not consistent and usually, was very low.

REACTION OF $[IrCl(CO)(PPh_3)_2]$ WITH $(PhCO)_2CN_2$

There was no apparent reaction between the diazoalkane molecule and Vaska's complex, $[IrCl(CO)(PPh_3)_2]$. A similar lack of reactivity was also observed between Vaska's complex and $N_2C_5Cl_4$.[1]

REACTION OF $[IrCl(C_8H_{14})]_2]_2$, PPh_3 AND $(Ph_2CO)_2CN_2$

Both infrared and $^{31}P\{^1H\}$ spectra of the solution mixture indicate that there are several species present in the mixture from the outset. In addition, the reactions involved are solvent dependent, since different $^{31}P\{^1H\}$ NMR peaks were observed in the toluene and CH_2Cl_2 solutions. Only one compound was isolated pure as a solid, compound 2, which was determined to be $[IrCl\{(C_6H_4)COCC(C_6H_5)OPPh_2)(PPh_3)_2]$ through an X-ray structural determination (*vide supra*). The three bands in the infrared spectrum at 1636, 1577 and 1546 cm^{-1} are not unlike the ν_{CO} bands observed in the uncomplexed aliphatic diazo molecule, although in 2 these are now the result of one C=O group and a C=C group; the assignment of these bands cannot be made unambiguously. In the mass spectrum, the highest peak (974 m/e, assigned to $[IrCl(PPh_3)_2\{(PhCO)_2C\}]^+$) was the same as for compound 1 and the intact molecular ion (1251 m/e) was not observed. The fragmentation patterns between the two species 1 and 2 were not the same however, with the major peaks in 2

resulting from PPh_3 (262, base peak, PPh_3^+; 183, $PPh(C_6H_3)^+$) and Ph_2PO^+ (201 m/e). The tridentate ligand $\{(C_6H_4)COCC(C_6H_5)OPPh_2\}$ was not observed although the fragments, $(PhCO)_2CH_2^+$ (224), $(PhCO)_2CH^+$ (223) and Ph_2PO^+ (201 m/e) were evident.

REACTION OF $[RhCl(C_8H_{14})_2]_2$ WITH PPh_3 AND $(PhCO)_2CN_2$

Two products, 3 and 4, were obtained from this reaction. The infrared spectrum of 3 showed three bands at 1675, 1625 and 1605 cm^{-1}, significantly perturbed from those of the starting diazoalkane molecule. The mass spectral data showed a highest peak of 446 m/e, with no indication of the presence of a metal species, but both PPh_3 (262 m/e) and the carbene fragment from the diazoalkane molecule were present (224, $(PhCO)_2CH_2^+$; 223, $(PhCO)_2CH^+$; 105, base peak, $(PhCO)^+$). The $^{31}P\{^1H\}$ NMR spectrum also indicated that 3 was not a Rh complex, since a singlet was observed in the spectrum, with no Rh-P coupling. This compound was identified through elemental analysis as $Ph_3P=N_2C(COPh)_2$, a phosphazine. The formation of phosphazines is fairly common[44] and they are often used as a method of stabilizing aliphatic diazo molecules. Compound 3 has been prepared by Regitz through refluxing PPh_3 and $(PhCO)_2CN_2$ in ether for one minute.[45]

Complex 4, a white crystalline material, also appeared to be a metal-free species since the $^{31}P\{^1H\}$ NMR spectrum

again showed only a singlet at 18.2 ppm, with no Rh-P coupling. This compound was identified as $Ph_3P=C(COPh)_2$, a phosphorous ylide, through comparison of the infrared, $^{31}P\{^1H\}$ and mass spectra with those of an authentic sample,[46] kindly prepared by Dr. L. Vande Griende. The major peaks in the mass spectrum correspond to the ions $(Ph_3PC(COPh)_2)^+$ (484, parent), Ph_3PO^+ (277) and $(C_7H_7)^+$, (91 m/e, base peak). Compound 4 has previously been prepared[46] through reaction of the phosphorane ($Ph_3P=CH-COPh$) with the carboxylic anhydride $(PhCOO)_2O$.

No Rh-phosphorus complexes were observed in the $^{31}P\{^1H\}$ NMR spectrum of the reaction solution.

REACTION OF $[IrCl(C_8H_{14})_2]_2$ WITH $P(i\text{-}C_3H_7)_3$ AND $(PhCO)_2CN_2$

The yellow crystalline complex 5 had a parent peak in the mass spectrum of 326 m/e, which suggested that 5 was an organic compound, rather than an Ir complex. This was confirmed through elemental analysis, and 5 was identified as $(i\text{-}C_3H_7)_3P=N_2C(COPh)_2$, a phosphazine compound, analogous to compound 3. The major peaks in the mass spectrum correspond to $[(i\text{-}C_3H_7)H_2P=N_2C(COPh)_2]^+$ (326, highest peak), $[(i\text{-}C_3H_7)HP=N_2C(COPh)_2]^+$ (325, base peak), $P(i\text{-}C_3H_7)_3^+$ (160) and $(PhCO)^+$ (105 m/e). The bands in the infrared spectrum are assigned as 1675 cm^{-1}, ν_{CN}; 1610, 1600 and 1575 cm^{-1}, ν_{CO}. No iridium-containing species was isolated.

REACTION OF $[RhCl(PPh_3)_2]_2$ AND $[RhCl(PPh_3)_3]$ WITH $(PhCO)_2CN_2$

Although no compounds were isolated from this reaction, the $^{31}P\{^1H\}$ NMR results are useful in determining the reaction pathway. Of the two Rh species present, $[RhCl(PPh_3)_2]_2$ and $[RhCl(PPh_3)_3]$, only the monomer reacts with the diazoalkane molecule. The dimer resonance peaks remain unchanged, even after 1 week. The monomer reacts almost instantaneously to produce a new Rh species (6) ($\delta = 24.8$ ppm, doublet, $|^1J_{Rh-P}| = 117$ Hz), with equivalent phosphines, and an organic phosphine ($\delta = 18.2$ ppm, singlet), which has the same chemical shift as compound 4, and is presumed to be $Ph_3P = C(COPh)_2$. Within 24 h, all of 6 has converted into the phosphorous ylide, compound 4, and the only Rh containing species observed in the spectrum, is the dimer $[RhCl(PPh_3)_2]_2$, whose $^{31}P\{^1H\}$ NMR signal has remained unchanged.

CONCLUSIONS

The reaction between $[IrCl(N_2(PPh_3)_2]$ and $(PhCO)_2CN_2$ produced several different species, of which only one, compound 1, was isolated and characterized. This species is believed to be $[IrCl\{(OCPh)_2CN_2\}(PPh_3)_2]$, in which the diazoalkane ligand is chelated through the two ketonic oxygen atoms. Tulip and Ibers[47] reported that for the synthesis of $[IrClH\{\eta^3\text{-}C_3H_4(1\text{-}C_6H_5)\}(PPh_3)_2]$, using $[IrCl(C_8H_{14})_2]_2$ with PPh_3 to produce *in situ* the species

"$IrCl(PPh_3)_2$" as the starting material was much more convenient than that using $[IrCl(N_2)(PPh_3)_2]$ and resulted in higher yields, shorter reaction times and cleaner products. Consequently the $[IrCl(C_8H_{14})_2]_2$ route was used in this study, in hopes that it would again result in cleaner, more convenient reactions. However, the reaction of $[IrCl(C_8H_{14})_2]_2$ with PPh_3 and $(PhCO)_2CN_2$ was found to be even more complex than the reaction between $[IrCl(N_2)(PPh_3)_2]$ and $(PhCO)_2CN_2$, as observed from the $^{31}P\{^1H\}$ NMR spectra of the two reaction solutions. The $^{31}P\{^1H\}$ NMR spectrum for the $[IrCl(C_8H_{14})_2]_2$ reaction solution confirmed that complex 1 (-13.2 ppm) was formed by this route as well as by the reaction of $[IrCl(N_2)(PPh_3)_2]$. However there were several other species observed in the former route which were not observed in the latter. Compound 1 was not isolated from the $[IrCl(C_8H_{14})_2]_2$ reaction, instead only complex 2 was obtained as a pure solid, and only in small quantities. Complex 2, in contrast to the chelating diazoalkane structure of 1, contained the novel ligand $(Ph_2POC(C_6H_5)CCO(C_6H_4))$, formed through the condensation of the carbene fragment $(Ph_2CO)_2C$, (which resulted from the loss of N_2 from the starting diazoalkane molecule) and a diphenylphosphine group. It is likely that this product resulted from an excess of PPh_3 in the reaction mixture, and as such we would expect that complex 2 would not be formed in the reaction of $[IrCl(N_2)(PPh_3)_2]$ with the diazoalkane molecule,

since there is no free PPh_3 present in this reaction. Unlike the reactions reported by Tulip and Ibers,[47] the above two reaction routes involving dibenzoyldiazomethane are not comparable.

In contrast to the various species produced in the reaction of $[IrCl(C_8H_{14})_2]_2$ with PPh_3 and $(PhCO)_2CN_2$, only two species, 3 and 4 were formed in the analogous reaction with $[RhCl(C_8H_{14})_2]_2$. Both 3 and 4 are organic phosphorus compounds, neither of which was observed in the $^{31}P\{^1H\}$ NMR spectrum of the iridium reaction solution. If PPh_3 and $(PhCO)_2CN_2$ are reacted together, in the absence of a metal compound, only complex 3, the phosphazine $(Ph_3P=N_2C-(COPh)_2)$, is formed. This suggests that the formation of 3 in the $[RhCl(C_8H_{14})_2]_2$ reaction may be the result of an excess of triphenylphosphine, while the formation of 4, the phosphorus ylide $[Ph_3P=C(COPh)_2]$, may have been catalyzed by the rhodium complex. In agreement with this, a phosphazine was not observed in the reaction of $[RhCl(PPh_3)_3]$ with $(PhCO)_2CN_2$, in which there was no excess phosphine, although the phosphorus ylide 4 was observed. In fact, compound 4 resulted from an intermediate Rh species 6, which lasted for less than 24 h, and may have been a rhodium-diazoalkane complex. Overall, it appears therefore that the rhodium species catalyzed the formation of the phosphorus ylide, 4, through coordination of the diazoalkane molecule and subsequent loss of N_2 from the diazoalkane molecule, generating

the carbene which further reacts with a coordinated phosphine ligand.

The reaction of $[IrCl(C_8H_{14})_2]_2$ with $P(i\text{-}C_3H_7)_3$ and $(PhCO)_2CN_2$ yielded only a phosphazine, compound 5, $(i\text{-}C_3H_7)_3P{=}N_2C(COPh)_2$, which was observed after 5 days. It is not certain when compound 5 is initially formed, as the solution was not monitored earlier than this. It is not likely that this phosphazine formation is catalyzed by the presence of the iridium complex, as no similar phosphazine was observed in the analogous reaction with PPh_3. Furthermore, a phosphorus ylide, such as was found to be catalyzed by the rhodium metal species, was not observed.

The products formed from the reaction of dibenzoyldiazomethane with various Rh and Ir complexes are quite diverse. In particular, the diazoalkane molecule reacted very differently with the iridium species than with the rhodium complexes. With the latter, when reactions were observed (surprisingly no reaction was observed for $[RhCl(PPh_3)_2]_2$), phosphorus ylides were produced, presumably *via* metal carbene intermediates. In contrast, the iridium species did not result in phosphorus ylide formation. Significantly the only carbene-like species observed in the iridium reactions, compound 2, resulted presumably, from an initial metal-carbene compound, which subsequently formed the unusual tridentate ligand described, rather than forming a phosphorus ylide. It may be that with both rhodium and

iridium species, metal-carbene complexes are formed initially, but that these subsequently react in different ways for the two metals. The only diazoalkane-containing species isolated was compound 1, an iridium complex having the diazoalkane ligand chelated through both α-ketone groups. In the presence of free phosphine, the production of phosphazine was observed; however these were not metal catalyzed and could be prepared in the absence of a metal species. Finally, we note that in the iridium reactions, only a small number of the species present were identified, owing to the complexities of the reactions. In particular the reaction in which the species "$IrCl(PPh_3)_2$" was generated *in situ* from the cyclooctene complex, was extremely complex and surprisingly different from the analogous reaction involving $[IrCl(N_2)(PPh_3)_2]$.

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Appendix I: Programs Used in Crystal Structure Solution, Refinement and Analysis.

Author	Program	Description
Northwestern University	AGNOST	Absorption correction program using Gaussian Integration.
J.A. Ibers A.P. Gaughan	CELREF	Refines crystal alignment and cell parameters.
S.K. Dwight	DATABL	Outputs tables of position and thermal parameters for publication.
A. Zalkin	FORDAP	Fourier summation for Patterson or Fourier maps.
P.D. Cradwick	HATOM	Calculates positions of hydrogen atoms attached to atoms which are sp^3 or sp^2 hybridized.
M.J. Bennett B. Foxman	MMMR	Calculates starting parameters for rigid bodies and hindered rotors.
G. Germain P. Main M.M. Woolfson	MULTAN	General direct methods program.
P. Main C.T. Grainger	NORMAL	Calculates E's, does Wilson statistics. For input to MULTAN.
M.E. Pippy F.R. Ahmed	NRC-22	Calculates least-squares planes.

Appendix I, continued

Author	Program	Description
W. Busing H.A. Levy	ORFFE	Calculates bond lengths, angles and associated standard deviations. Modified by W.L. Brooks and M. Elder for hindered rotors and rigid bodies.
C. Johnson	ORTEP	Thermal ellipsoids plotting program.
M.J. Bennett	PMMO	Transforms raw data to intensities, applying corrections.
A.P. Gaughan	PRCNTA	Molecular weight, % composition, density, absorption coefficient calculations from formula and cell.
M. Cowie	PUBE	Sorts data according to any desired sequence of h, k or l.
R.C. Elder	PUBTAB	Prints structure factor amplitude tables, modified by S.K. Dwight for use on the page printer.
G. Germain P. Main M.M. Woolfson	RECYCL	Calculates starting phases to be input to MULTAN once a partial structure is available.

Appendix I, continued

Author	Program	Description
S.K. Dwight	RIGIDH	Calculated rigid body parameters for hydrogen atoms.
C.T. Prewitt	SFLS5	Structure factor calculation and least-squares refinement of parameters. Modified by B.M. Foxman and M.J. Bennett for rigid body routine, and by W.L. Hutcheon and M.J. Bennett for the hindered rotor.
S.L. Lawton	TRACERA	General Cell Reduction Program.

Appendix II: Structure Factor Amplitudes for $[Cp_2W(NH_2NPh)][BF_4]$, $(PhCOCN_2COPh)$, $(PhCOCN_2Ph)$ and $[IrCl((C_8H_4)COC(Ph)OPPh_2)(PPh_3)_2]\cdot C_6H_5CH_3$.

Table 27. 10*(Fobs vs. Fcal) for [Cp2W(NH2NPh)][BF4].

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
H = -9**				-4	7	156	146	-6	2	218	204	-2	11	118	106
-4	4	129	152	-4	9	166	141	-6	3	258	278	-2	12	126	144
-4	6	157	163	-4	10	244	241	-6	5	275	270	-2	13	135	143
-4	7	172	188	-4	12	88	41	-6	6	230	235	-2	14	334	346
-4	8	94	101	-4	13	123	121	-6	7	233	237	-2	16	135	126
-3	1	132	129	-4	14	210	199	-6	9	273	266	-2	17	107	110
-3	2	188	198	-3	1	178	188	-6	10	169	173	-2	18	197	185
-3	4	194	207	-3	2	162	176	-6	11	136	150	-1	1	110	79
-3	5	146	158	-3	4	361	351	-6	13	205	191	-1	2	99	130
-3	6	156	169	-3	5	180	173	-6	14	119	108	-1	4	594	584
-3	8	206	191	-3	6	115	107	-5	1	373	398	-1	6	118	90
-3	9	118	122	-3	7	175	137	-5	3	240	220	-1	7	113	96
-2	2	235	225	-3	8	434	405	-5	4	372	344	-1	8	596	559
-2	3	114	109	-3	9	172	170	-5	5	291	288	-1	9	109	121
-2	4	166	170	-3	11	112	109	-5	7	258	260	-1	10	126	134
-2	6	281	277	-3	12	275	282	-5	8	372	353	-1	12	438	444
-2	7	126	135	-3	15	81	84	-5	9	129	108	-1	14	203	179
-2	8	164	185	-2	2	412	415	-5	11	187	198	-1	15	103	79
-2	9	94	56	-2	3	154	145	-5	12	191	184	-1	16	244	266
-2	10	222	212	-2	4	209	223	-5	15	208	201	-1	18	117	115
-2	11	78	80	-2	6	430	410	-5	16	120	124	0	2	780	773
-1	2	229	246	-2	7	121	114	-4	1	139	145	0	6	599	564
-1	4	301	303	-2	8	96	53	-4	2	428	425	0	8	101	61
-1	6	138	145	-2	9	142	93	-4	3	274	291	0	10	503	474
-1	8	321	319	-2	10	435	407	-4	5	169	154	0	12	126	111
-1	9	86	105	-2	11	136	129	-4	6	465	461	0	14	310	306
-1	10	108	110	-2	14	273	262	-4	7	145	138	0	16	151	153
-1	12	236	220	-2	15	110	86	-4	9	259	249	0	18	226	221
0	2	294	291	-1	1	94	85	-4	10	400	377	**H = -6****			
0	4	171	189	-1	2	206	239	-4	11	97	95	-9	1	186	191
0	6	317	307	-1	4	506	474	-4	13	241	230	-9	3	223	223
0	8	114	133	-1	5	143	126	-4	14	228	215	-9	5	148	161
0	10	287	285	-1	6	96	85	-4	16	124	114	-9	7	204	195
H = -8**				-1	8	441	398	-4	17	115	113	-8	1	242	231
-6	2	174	167	-1	11	102	70	-3	1	285	260	-8	2	118	105
-6	3	244	280	-1	12	336	342	-3	2	148	139	-8	3	232	239
-6	5	127	113	-1	13	86	66	-3	3	133	112	-8	5	302	290
-6	6	168	173	-1	16	236	226	-3	4	603	573	-8	6	134	144
-6	7	192	197	0	2	444	465	-3	5	271	256	-8	7	127	153
-6	9	129	121	0	4	203	189	-3	6	101	103	-8	9	282	288
-6	10	120	116	0	6	466	450	-3	7	150	124	-8	10	102	90
-5	1	243	248	0	10	438	421	-3	8	501	476	-7	1	348	360
-5	2	85	83	0	14	301	285	-3	10	174	146	-7	3	328	321
-5	3	101	94	**H = -7****				-3	11	185	195	-7	4	260	247
-5	4	235	230	-8	3	186	190	-3	12	377	378	-7	5	210	206
-5	5	273	260	-8	5	159	150	-3	13	101	94	-7	7	363	336
-5	7	157	147	-8	7	141	163	-3	14	175	160	-7	8	180	171
-5	8	241	213	-7	1	266	281	-3	15	176	170	-7	9	138	142
-5	9	174	170	-7	3	202	204	-3	16	220	237	-7	11	318	329
-5	11	147	147	-7	4	176	161	-3	18	134	115	-7	12	115	116
-5	12	159	153	-7	5	213	225	-2	2	718	681	-7	14	95	83
-5	13	100	105	-7	7	244	232	-2	3	195	206	-6	1	273	266
-4	2	272	268	-7	8	138	122	-2	4	104	82	-6	2	305	303
-4	3	252	260	-7	9	156	160	-2	6	593	564	-6	3	363	370
-4	4	170	151	-7	11	212	210	-2	7	189	169	-6	5	412	380
-4	5	125	106	-7	12	112	117	-2	8	133	111	-6	6	304	287
-4	6	326	322	-6	1	143	154	-2	10	529	499	-6	7	217	207

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
H = -6**				-2	6	853	813	-7	8	137	164	-3	3	708	637
-6	8	157	140	-2	7	100	111	-7	9	100	52	-3	4	880	860
-6	9	395	369	-2	8	118	119	-7	10	170	182	-3	6	384	423
-6	10	244	232	-2	9	237	217	-7	11	370	384	-3	7	558	520
-6	12	100	98	-2	10	571	545	-7	12	127	144	-3	8	654	626
-6	13	239	236	-2	12	350	327	-7	13	91	78	-3	10	327	326
-6	14	182	183	-2	13	181	164	-7	14	105	128	-3	11	354	344
-5	1	345	340	-2	14	336	326	-7	15	237	218	-3	12	458	449
-5	3	357	346	-2	16	298	291	-6	1	564	536	-3	14	347	338
-5	4	486	474	-2	17	145	128	-6	2	418	405	-3	15	159	164
-5	5	250	224	-2	18	165	194	-6	3	329	334	-3	16	196	198
-5	6	180	140	-2	20	159	173	-6	4	203	187	-3	17	110	130
-5	7	327	304	-1	1	113	98	-6	5	548	538	-3	18	285	295
-5	8	300	305	-1	3	97	73	-6	6	417	415	-3	19	111	112
-5	10	171	168	-1	4	949	933	-6	7	176	178	-2	1	328	336
-5	11	334	357	-1	5	184	191	-6	8	162	153	-2	2	1125	1080
-5	12	324	304	-1	6	223	217	-6	9	398	384	-2	3	203	195
-5	13	99	75	-1	7	94	113	-6	10	248	218	-2	4	370	350
-5	14	93	83	-1	8	742	749	-6	12	228	223	-2	5	559	544
-5	15	210	198	-1	10	382	381	-6	13	392	376	-2	6	961	957
-5	16	124	132	-1	11	126	112	-6	14	141	141	-2	7	121	105
-4	1	289	274	-1	12	430	444	-6	16	155	157	-2	8	636	644
-4	2	631	608	-1	14	300	296	-6	17	160	183	-2	9	280	293
-4	3	346	319	-1	16	250	233	-5	1	337	337	-2	10	653	673
-4	5	405	386	-1	18	255	255	-5	2	255	261	-2	12	507	500
-4	6	524	506	-1	20	124	123	-5	3	541	484	-2	13	196	179
-4	7	198	198	0	2	788	733	-5	4	562	553	-2	14	351	356
-4	8	164	126	0	4	158	141	-5	5	287	265	-2	16	309	314
-4	9	240	237	0	6	805	804	-5	6	242	250	-2	17	100	104
-4	10	384	386	0	8	240	235	-5	7	580	556	-2	18	142	144
-4	12	182	152	0	10	676	673	-5	8	330	298	-2	20	247	238
-4	13	201	222	0	12	375	374	-5	9	157	150	-1	1	366	340
-4	14	300	289	0	14	301	293	-5	10	182	168	-1	2	422	475
-4	16	185	178	0	16	353	303	-5	11	370	360	-1	3	362	359
-4	17	208	195	0	18	144	168	-5	12	284	257	-1	4	1031	986
-4	18	141	123	0	20	185	199	-5	14	281	283	-1	5	88	75
-3	1	240	236	**H = -5****				-5	15	221	219	-1	6	558	597
-3	3	224	218	-10	5	254	262	-5	16	184	173	-1	7	305	282
-3	4	816	788	-9	1	167	205	-5	18	171	164	-1	8	1110	1084
-3	5	208	191	-9	3	319	328	-4	1	342	343	-1	10	625	614
-3	6	215	209	-9	7	328	343	-4	2	750	723	-1	12	446	441
-3	7	317	321	-9	11	263	259	-4	3	274	254	-1	14	434	461
-3	8	546	581	-8	1	503	482	-4	4	210	193	-1	16	197	175
-3	9	147	121	-8	2	136	123	-4	5	445	462	-1	18	364	347
-3	10	284	282	-8	3	195	195	-4	6	638	646	0	2	1223	1223
-3	11	238	206	-8	5	477	462	-4	8	308	285	0	4	609	592
-3	12	436	426	-8	6	135	126	-4	9	467	473	0	6	1272	1271
-3	14	183	199	-8	8	122	105	-4	10	368	367	0	8	621	627
-3	15	256	242	-8	9	352	353	-4	12	396	381	0	10	629	627
-3	16	253	253	-8	12	89	80	-4	13	405	371	0	12	638	627
-3	17	91	63	-8	13	238	276	-4	14	306	322	0	14	252	261
-3	18	172	178	-7	1	270	271	-4	16	244	234	0	16	365	386
-3	19	94	94	-7	3	545	529	-4	17	155	158	0	18	140	133
-2	2	922	878	-7	4	251	237	-4	18	108	106	0	20	280	283
-2	3	200	205	-7	5	326	314	-4	19	106	93	**H = -4****			
-2	4	159	132	-7	6	159	168	-3	1	402	398	-10	1	361	361
-2	5	276	259	-7	7	493	500	-3	2	370	383	-10	5	303	299

Table 27. Continued

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
H = -4**				-5	14	373	380	-2	20	290	290	-7	9	274	290
-10	9	242	280	-5	15	316	333	-1	1	223	232	-7	10	195	205
-9	1	146	125	-5	17	172	173	-1	2	891	875	-7	11	489	508
-9	3	537	518	-5	18	216	230	-1	3	458	438	-7	12	104	119
-9	7	381	389	-5	19	85	117	-1	4	1353	1365	-7	13	275	265
-9	9	101	101	-4	1	841	828	-1	5	121	93	-7	14	149	151
-9	11	269	270	-4	2	920	931	-1	6	1099	1094	-7	15	216	213
-8	1	649	618	-4	3	300	263	-1	7	153	172	-7	17	202	217
-8	2	152	148	-4	4	758	798	-1	8	832	877	-6	1	898	853
-8	5	528	541	-4	5	872	841	-1	10	846	929	-6	2	419	377
-8	8	111	119	-4	6	542	538	-1	12	360	333	-6	4	423	412
-8	9	461	472	-4	7	125	112	-1	13	94	8	-6	5	774	790
-8	11	132	139	-4	8	658	690	-1	14	695	665	-6	6	241	235
-8	13	275	300	-4	9	621	625	-1	16	178	198	-6	7	379	385
-8	15	130	125	-4	10	401	395	-1	18	382	396	-6	8	450	448
-7	1	283	251	-4	11	171	153	0	2	1286	1285	-6	9	565	559
-7	2	188	151	-4	12	391	405	0	4	1032	1073	-6	10	313	298
-7	3	740	719	-4	13	428	433	0	6	907	915	-6	11	382	389
-7	4	240	232	-4	14	163	144	0	8	1153	1221	-6	12	301	300
-7	6	205	205	-4	15	135	153	0	10	866	835	-6	13	306	323
-7	7	698	684	-4	16	407	399	0	12	821	837	-6	15	298	308
-7	8	233	210	-4	17	150	144	0	14	252	252	-6	16	239	242
-7	10	133	152	-4	19	133	139	0	16	581	550	-6	17	153	166
-7	11	349	356	-4	20	223	227	0	20	334	328	-5	2	639	591
-7	12	127	123	-3	1	206	185	**H = -3****				-5	3	858	868
-7	13	175	163	-3	2	558	569	-11	3	294	314	-5	4	534	569
-7	14	159	161	-3	3	647	589	-10	1	411	417	-5	5	383	398
-7	15	272	269	-3	4	912	855	-10	5	376	370	-5	6	804	802
-7	17	126	143	-3	6	700	676	-10	7	144	137	-5	7	794	817
-6	1	683	648	-3	7	485	496	-10	9	277	297	-5	8	194	216
-6	2	493	495	-3	8	585	611	-10	11	139	159	-5	9	380	404
-6	3	140	122	-3	10	744	770	-9	3	502	496	-5	10	665	695
-6	4	350	360	-3	11	394	418	-9	4	101	80	-5	11	561	563
-6	5	757	730	-3	12	322	323	-9	5	199	180	-5	12	99	112
-6	6	326	348	-3	13	130	142	-9	7	415	419	-5	13	368	385
-6	8	330	328	-3	14	594	600	-9	9	193	170	-5	14	330	348
-6	9	712	706	-3	15	307	306	-9	11	324	346	-5	15	219	233
-6	10	202	183	-3	16	144	174	-9	13	174	179	-5	17	258	276
-6	12	221	249	-3	17	105	86	-8	1	653	655	-5	18	264	257
-6	13	323	316	-3	18	275	283	-8	4	125	122	-4	1	1092	1047
-6	14	131	127	-3	19	91	81	-8	5	637	627	-4	2	825	746
-6	15	203	222	-3	21	109	87	-8	6	104	92	-4	3	245	242
-6	16	197	216	-2	1	696	682	-8	7	268	267	-4	4	953	996
-6	17	172	165	-2	2	1453	1476	-8	8	106	84	-4	5	772	794
-5	1	223	200	-2	3	165	164	-8	9	500	500	-4	6	303	286
-5	2	459	466	-2	4	938	984	-8	10	122	127	-4	7	333	324
-5	3	678	656	-2	5	779	771	-8	11	174	206	-4	8	946	969
-5	4	478	449	-2	6	910	927	-8	12	109	76	-4	9	590	589
-5	5	144	131	-2	7	311	337	-8	13	215	235	-4	10	229	204
-5	6	466	444	-2	8	864	922	-8	15	206	213	-4	11	421	410
-5	7	643	643	-2	9	273	256	-7	2	213	206	-4	12	684	701
-5	8	487	491	-2	10	626	604	-7	3	746	752	-4	13	340	351
-5	9	176	173	-2	12	743	760	-7	4	317	318	-4	15	368	385
-5	10	373	356	-2	13	207	231	-7	5	228	226	-4	16	413	410
-5	11	534	522	-2	14	292	311	-7	6	197	214	-4	17	191	204
-5	12	203	217	-2	16	470	458	-7	7	540	551	-4	19	191	171
-5	13	163	198	-2	17	114	104	-7	8	143	187	-4	20	218	224

Table 27. Continued

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
H = -3**				0	16	779	758	-6	7	561	550	-3	21	155	147
-3	2	1297	1274	0	20	367	361	-6	8	497	486	-2	1	143	143
-3	3	841	874	**H = -2****				-6	9	347	356	-2	2	292	297
-3	4	784	813	-11	1	133	118	-6	11	408	421	-2	3	74	83
-3	5	100	120	-11	3	313	320	-6	12	435	423	-2	4	1397	1447
-3	6	1363	1446	-11	5	115	114	-6	13	273	281	-2	5	516	559
-3	7	616	621	-11	7	228	260	-6	15	398	400	-2	6	355	355
-3	8	373	375	-10	1	502	488	-6	16	222	237	-2	7	174	237
-3	9	327	339	-10	3	221	201	-6	17	101	100	-2	8	1154	1288
-3	10	1012	1046	-10	5	369	392	-5	1	400	393	-2	9	138	74
-3	11	380	381	-10	7	234	239	-5	2	1109	1180	-2	11	376	370
-3	12	135	159	-10	9	273	286	-5	3	1030	1031	-2	12	1076	1066
-3	13	275	286	-10	10	89	65	-5	4	499	485	-2	14	111	103
-3	14	520	552	-10	11	242	247	-5	5	544	555	-2	15	267	276
-3	15	285	280	-9	1	153	137	-5	6	890	949	-2	16	502	514
-3	17	169	169	-9	2	136	126	-5	7	570	589	-2	18	163	188
-3	18	377	378	-9	3	538	557	-5	9	558	561	-2	19	99	125
-3	19	103	81	-9	5	233	226	-5	10	621	658	-2	20	304	303
-3	21	119	112	-9	7	446	450	-5	11	338	337	-1	1	697	668
-2	1	788	837	-9	8	99	56	-5	13	490	471	-1	2	2492	2636
-2	2	1151	1126	-9	9	394	386	-5	14	484	475	-1	3	369	373
-2	3	469	496	-9	11	284	306	-5	15	148	141	-1	4	332	351
-2	4	1138	1195	-9	13	263	274	-5	16	113	80	-1	6	1673	1777
-2	5	313	317	-8	1	782	743	-5	17	351	351	-1	7	271	267
-2	6	709	706	-8	3	281	256	-5	18	268	264	-1	8	368	330
-2	8	1343	1364	-8	4	170	165	-4	1	521	523	-1	10	1406	1442
-2	9	121	150	-8	5	491	526	-4	2	574	553	-1	12	247	226
-2	10	305	306	-8	6	101	93	-4	3	354	357	-1	13	176	182
-2	11	108	144	-8	7	354	352	-4	4	1306	1343	-1	14	811	848
-2	12	814	880	-8	8	167	153	-4	5	832	879	-1	16	305	333
-2	13	205	210	-8	9	353	377	-4	6	205	211	-1	17	138	124
-2	15	145	177	-8	10	116	141	-4	7	825	875	-1	18	560	541
-2	16	663	649	-8	11	389	398	-4	8	1119	1170	-1	20	212	226
-2	17	125	133	-8	12	146	132	-4	9	459	452	0	2	456	439
-2	19	121	82	-8	13	259	279	-4	11	500	516	0	4	1600	1629
-2	20	279	283	-8	15	269	267	-4	12	639	664	0	6	623	673
-1	1	137	138	-7	1	259	269	-4	13	284	292	0	8	1253	1376
-1	2	1339	1381	-7	2	223	271	-4	15	370	367	0	12	1326	1329
-1	3	138	120	-7	3	742	756	-4	16	373	397	0	14	381	349
-1	4	1068	1076	-7	4	170	175	-4	17	91	45	0	16	770	795
-1	6	1150	1249	-7	5	332	353	-4	19	249	242	0	18	213	221
-1	7	70	50	-7	6	291	314	-4	20	215	226	0	20	326	324
-1	8	498	492	-7	7	515	529	-3	2	1525	1572	**H = -1****			
-1	9	127	119	-7	9	385	397	-3	3	682	686	-11	1	157	161
-1	10	1263	1312	-7	10	270	285	-3	4	360	345	-11	3	283	264
-1	12	255	254	-7	11	295	314	-3	5	429	444	-11	5	262	266
-1	13	99	79	-7	12	191	181	-3	6	1276	1351	-11	7	187	206
-1	14	916	944	-7	13	356	369	-3	7	627	659	-10	1	416	430
-1	15	136	157	-7	14	222	219	-3	9	415	418	-10	3	322	339
-1	18	492	490	-7	15	132	126	-3	10	1066	1123	-10	5	375	391
-1	20	113	97	-7	17	247	264	-3	11	298	315	-10	7	315	334
0	2	768	789	-6	1	857	859	-3	13	383	390	-10	9	215	218
0	4	1295	1334	-6	2	444	412	-3	14	608	610	-10	11	334	343
0	6	1189	1181	-6	3	460	451	-3	16	152	147	-9	1	335	321
0	8	1291	1277	-6	4	654	617	-3	17	320	309	-9	3	576	564
0	10	103	169	-6	5	685	702	-3	18	381	389	-9	5	447	458
0	12	1023	1096	-6	6	282	282	-3	20	104	121	-9	6	119	108

Table 27. Continued

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
H = -1**				-5	13	444	454	-2	19	149	140	-8	15	298	313
-9	7	362	394	-5	14	455	459	-2	20	252	250	-7	1	676	687
-9	8	107	76	-5	16	179	176	-1	1	345	345	-7	2	415	406
-9	9	440	441	-5	17	321	320	-1	2	2342	2546	-7	3	457	460
-9	10	116	138	-5	18	236	242	-1	3	600	637	-7	4	316	304
-9	11	147	133	-4	1	1114	1103	-1	4	201	275	-7	5	733	763
-9	12	92	81	-4	2	89	121	-1	5	116	118	-7	6	396	377
-9	13	358	363	-4	3	691	755	-1	6	1525	1559	-7	7	333	320
-8	1	661	703	-4	4	1395	1486	-1	7	116	115	-7	8	167	134
-8	3	518	524	-4	5	756	721	-1	8	258	249	-7	9	605	596
-8	4	268	243	-4	6	410	393	-1	9	449	481	-7	10	228	221
-8	5	536	535	-4	7	645	642	-1	10	1262	1370	-7	11	129	113
-8	7	434	437	-4	8	994	1043	-1	12	456	522	-7	13	480	472
-8	8	117	128	-4	9	369	376	-1	13	153	124	-7	14	193	166
-8	9	346	355	-4	10	238	224	-1	14	826	794	-7	16	111	85
-8	11	483	491	-4	11	509	506	-1	16	443	427	-6	0	544	596
-8	12	177	192	-4	12	682	688	-1	18	347	353	-6	1	931	936
-8	15	291	311	-4	13	188	179	-1	20	278	291	-6	3	728	731
-7	1	523	500	-4	14	167	199	0	2	819	776	-6	4	869	866
-7	2	416	431	-4	15	407	397	0	4	3453	3950	-6	5	457	475
-7	3	654	670	-4	16	450	445	0	6	225	217	-6	6	287	302
-7	5	504	490	-4	18	206	201	0	8	1983	2158	-6	7	633	664
-7	6	422	426	-4	19	218	231	0	10	501	522	-6	8	507	493
-7	7	406	406	-4	20	190	207	0	12	1212	1201	-6	9	232	222
-7	9	421	423	-3	2	1076	1125	0	14	362	377	-6	10	204	220
-7	10	271	252	-3	3	1249	1316	0	16	428	418	-6	11	621	602
-7	11	177	183	-3	4	139	143	0	18	436	462	-6	12	369	345
-7	13	465	471	-3	5	541	565	0	20	317	299	-6	14	222	221
-7	14	252	250	-3	6	1349	1431	**H = 0****				-6	15	409	404
-7	17	271	276	-3	7	483	493	-11	1	280	289	-6	16	199	208
-6	1	839	852	-3	9	783	834	-11	2	102	88	-6	18	136	121
-6	3	802	848	-3	10	852	904	-11	3	203	214	-5	1	952	1003
-6	4	747	767	-3	12	258	261	-11	5	247	265	-5	2	1229	1223
-6	5	565	549	-3	13	389	376	-11	7	114	112	-5	3	897	893
-6	7	404	421	-3	14	649	629	-10	1	364	384	-5	4	266	262
-6	8	548	576	-3	16	241	237	-10	3	394	394	-5	5	1046	1102
-6	9	382	379	-3	17	235	220	-10	5	248	234	-5	6	980	1009
-6	10	136	122	-3	18	333	308	-10	7	457	461	-5	7	263	253
-6	11	447	459	-3	20	208	202	-10	9	92	114	-5	8	275	264
-6	12	348	370	-2	1	83	96	-10	11	298	304	-5	9	551	561
-6	13	161	143	-2	2	1004	931	-9	1	556	541	-5	10	573	579
-6	14	104	93	-2	3	167	176	-9	3	306	307	-5	11	182	176
-6	15	398	387	-2	4	1808	1891	-9	5	613	630	-5	12	371	349
-6	16	253	278	-2	5	624	574	-9	7	275	294	-5	13	554	542
-6	18	85	86	-2	6	173	157	-9	9	493	493	-5	14	444	437
-5	1	561	544	-2	7	673	678	-9	11	88	67	-5	16	256	250
-5	2	1031	1080	-2	8	1425	1505	-9	13	316	318	-5	17	272	278
-5	3	796	836	-2	9	289	306	-8	0	183	194	-5	18	154	169
-5	4	241	225	-2	10	243	246	-8	1	532	533	-5	19	95	110
-5	5	764	806	-2	11	336	360	-8	3	675	694	-4	0	1220	1250
-5	6	1251	1274	-2	12	858	893	-8	4	142	164	-4	1	926	907
-5	7	517	517	-2	13	124	103	-8	5	378	375	-4	2	471	432
-5	8	92	128	-2	14	275	302	-8	7	630	625	-4	3	852	819
-5	9	605	603	-2	15	203	195	-8	8	141	195	-4	4	1405	1459
-5	10	649	612	-2	16	497	471	-8	9	188	195	-4	5	684	753
-5	11	224	228	-2	17	175	161	-8	11	492	478	-4	6	299	297
-5	12	215	209	-2	18	303	310	-8	12	161	155	-4	7	977	1024

Table 27. Continued

K	L	FOBS	FCAL
H = 0**			
-4	8	1242	1256
-4	9	219	199
-4	10	313	329
-4	11	593	593
-4	12	631	613
-4	14	434	417
-4	15	370	343
-4	16	358	361
-4	17	111	117
-4	18	274	281
-4	19	166	175
-3	1	798	829
-3	2	971	1031
-3	3	897	919
-3	5	1063	1137
-3	6	1451	1535
-3	8	130	139
-3	9	612	556
-3	10	979	974
-3	11	263	289
-3	12	498	473
-3	13	395	396
-3	14	504	509
-3	16	387	390
-3	17	205	206
-3	18	221	235
-3	19	108	113
-3	20	260	260
-2	0	2876	2868
-2	1	1409	1457
-2	2	754	735
-2	3	215	215
-2	4	1514	1586
-2	5	911	921
-2	6	365	375
-2	7	561	587
-2	8	1432	1443
-2	9	183	181
-2	10	534	524
-2	11	444	453
-2	12	824	830
-2	14	496	499
-2	15	192	202
-2	16	416	406
-2	18	405	397
-2	20	142	146
-1	1	461	464
-1	2	2446	2823
-1	3	745	786
-1	4	114	119
-1	5	209	225
-1	6	1912	2063
-1	7	168	141
-1	8	747	813
-1	9	255	224
-1	10	1354	1357
-1	11	106	106
-1	12	744	724
-1	13	190	202
-1	14	573	576
-1	16	315	329
-1	18	262	249
-1	20	336	330
0	2	491	462
0	4	2127	2372
0	6	737	805
0	8	1556	1546
0	10	918	876
0	12	933	963
0	14	618	634
0	16	540	506
0	18	384	386
0	20	165	166
H = 1**			
-11	1	311	329
-11	3	144	128
-11	5	286	285
-10	1	225	215
-10	3	508	485
-10	6	137	118
-10	7	389	382
-9	1	672	648
-9	3	188	191
-9	5	545	521
-9	9	506	506
-9	10	113	83
-8	0	222	202
-8	1	380	332
-8	3	694	650
-8	4	193	218
-8	7	741	726
-8	8	184	164
-8	11	532	509
-8	12	134	106
-7	1	946	930
-7	2	367	370
-7	3	309	298
-7	4	175	148
-7	5	760	767
-7	6	265	268
-7	7	103	96
-7	8	184	176
-7	9	758	732
-7	10	240	232
-7	13	438	438
-7	14	149	163
-7	15	111	133
-6	0	800	774
-6	1	473	460
-6	2	200	184
-6	3	986	997
-6	4	636	596
-6	5	218	205
-3	10	868	849
-6	6	483	481
-6	7	921	917
-6	8	446	403
-6	9	110	99
-6	10	246	221
-6	11	635	620
-6	12	327	324
-6	13	191	153
-6	14	218	215
-6	15	368	355
-6	16	140	128
-6	17	112	114
-5	0	420	380
-5	1	1311	1259
-5	2	1176	1184
-5	3	363	345
-5	4	253	248
-5	5	1099	1065
-5	6	892	884
-5	8	603	569
-5	9	906	898
-5	10	518	514
-5	12	374	377
-5	13	495	497
-5	14	323	303
-5	15	216	215
-5	16	305	299
-5	17	245	229
-5	18	110	97
-4	0	1355	1343
-4	1	625	595
-4	2	519	493
-4	3	1155	1192
-4	4	1488	1482
-4	5	83	75
-4	6	750	712
-4	7	1047	1013
-4	8	766	765
-4	9	143	149
-4	10	609	597
-4	11	582	538
-4	12	518	530
-4	14	557	529
-4	15	382	380
-4	16	198	187
-4	17	154	141
-4	18	281	279
-3	0	292	315
-3	1	828	776
-3	2	1549	1510
-3	3	258	250
-3	4	672	694
-3	5	970	880
-3	6	1329	1308
-3	8	1016	978
-3	9	620	651
-3	11	100	85
-3	12	625	635
-3	13	436	436
-3	14	417	402
-3	15	171	188
-3	16	486	464
-3	17	210	203
-3	18	89	106
-2	0	1857	1713
-2	1	459	400
-2	2	643	607
-2	3	467	440
-2	4	989	1024
-2	5	162	176
-2	6	1255	1194
-2	7	434	423
-2	8	1287	1334
-2	9	94	29
-2	10	963	950
-2	11	263	232
-2	12	598	576
-2	14	715	687
-2	15	303	302
-2	16	248	256
-2	18	384	369
-2	19	102	82
-1	0	585	628
-1	1	364	331
-1	2	3311	3473
-1	3	704	668
-1	4	1255	1237
-1	5	77	81
-1	6	1436	1443
-1	7	195	215
-1	8	942	977
-1	9	111	133
-1	10	983	924
-1	12	752	748
-1	13	158	141
-1	14	465	456
-1	16	603	595
-1	17	148	130
-1	18	267	263
-1	20	332	328
0	0	2378	2520
0	2	1601	1458
0	4	1585	1627
0	6	1190	1106
0	8	1504	1601
0	10	1170	1187
0	12	635	619
0	14	747	705
0	16	338	360
0	18	361	372
0	20	130	118
H = 2**			
-11	1	314	323

Table 27. Continued

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
H = 2**				-5	5	1073	1064	-2	10	1059	1023	-7	3	285	247
-10	3	408	422	-5	6	399	400	-2	11	323	323	-7	4	323	311
-10	7	323	313	-5	7	299	303	-2	12	293	255	-7	5	688	679
-9	1	611	602	-5	8	523	524	-2	13	151	186	-7	6	355	334
-9	2	154	111	-5	9	627	601	-2	14	660	640	-7	7	315	282
-9	3	110	63	-5	10	392	374	-2	15	186	176	-7	8	286	267
-9	5	551	518	-5	11	385	370	-2	16	122	106	-7	9	332	343
-9	6	149	159	-5	12	437	436	-2	17	166	190	-7	10	135	127
-9	7	102	65	-5	13	357	342	-2	18	423	421	-7	11	308	294
-9	9	395	383	-5	14	219	223	-1	0	1041	995	-7	12	217	204
-9	10	100	91	-5	15	254	238	-1	1	771	683	-7	13	220	223
-9	11	125	128	-5	16	274	258	-1	2	607	608	-6	0	438	490
-8	0	186	175	-5	17	196	190	-1	3	271	257	-6	2	438	432
-8	3	804	776	-4	0	1333	1331	-1	4	1167	1140	-6	3	785	770
-8	4	301	283	-4	1	194	199	-1	5	101	120	-6	4	327	320
-8	7	533	523	-4	2	962	877	-1	6	1278	1183	-6	6	468	461
-8	8	157	180	-4	3	1315	1236	-1	7	142	158	-6	7	546	523
-8	9	166	167	-4	4	897	913	-1	8	1523	1433	-6	8	157	171
-8	11	399	414	-4	5	299	284	-1	9	141	143	-6	9	408	414
-8	12	102	94	-4	6	782	736	-1	10	691	694	-6	10	335	327
-8	13	167	169	-4	7	922	825	-1	12	983	947	-6	11	316	286
-7	0	229	259	-4	8	456	462	-1	13	190	167	-6	12	123	150
-7	1	827	825	-4	9	183	138	-1	14	174	148	-6	13	312	304
-7	2	436	416	-4	10	786	748	-1	16	627	615	-6	14	246	239
-7	3	153	97	-4	11	518	504	-1	18	94	57	-5	0	724	691
-7	4	150	163	-4	12	282	293	0	0	1326	1352	-5	1	702	704
-7	5	768	730	-4	13	328	325	0	2	1002	958	-5	2	528	546
-7	6	286	273	-4	14	443	435	0	4	1156	1222	-5	3	111	109
-7	7	281	286	-4	15	245	256	0	6	1465	1487	-5	4	490	496
-7	8	181	167	-4	17	218	216	0	8	958	961	-5	5	723	679
-7	9	661	640	-3	0	1354	1353	0	10	998	979	-5	6	343	314
-7	10	238	238	-3	1	565	574	0	12	286	296	-5	7	323	323
-7	11	281	278	-3	2	1553	1519	0	14	676	679	-5	8	490	459
-7	12	141	151	-3	3	536	470	0	16	116	133	-5	9	426	402
-7	13	338	336	-3	4	1299	1242	0	18	508	518	-5	10	144	164
-7	14	119	112	-3	5	820	847	**H = 3****				-5	11	313	289
-6	0	608	586	-3	6	887	875	-11	1	301	318	-5	12	461	432
-6	1	193	194	-3	7	447	428	-10	3	360	375	-5	13	228	242
-6	2	409	364	-3	8	1011	976	-9	1	594	573	-5	15	230	246
-6	3	987	967	-3	9	466	466	-9	2	153	121	-4	0	938	1002
-6	4	639	607	-3	10	434	417	-9	3	208	174	-4	1	148	144
-6	5	152	133	-3	11	141	135	-9	5	478	464	-4	2	1086	1064
-6	6	263	244	-3	12	791	763	-9	6	103	81	-4	3	1009	940
-6	7	782	751	-3	13	320	301	-9	7	131	146	-4	4	632	647
-6	8	301	282	-3	14	169	149	-9	9	307	285	-4	5	304	255
-6	9	311	286	-3	15	285	266	-8	3	633	611	-4	6	683	640
-6	10	403	377	-3	16	521	505	-8	4	200	223	-4	7	597	603
-6	11	566	548	-3	17	210	198	-8	5	173	176	-4	8	160	169
-6	12	250	239	-2	0	747	656	-8	6	206	195	-4	9	325	313
-6	13	257	250	-2	2	1989	1916	-8	7	519	494	-4	10	507	515
-6	14	223	220	-2	3	286	270	-8	8	125	135	-4	11	283	267
-6	15	255	237	-2	4	1299	1325	-8	9	251	270	-4	12	155	153
-5	0	405	448	-2	5	180	169	-8	10	137	118	-4	13	297	293
-5	1	1050	1014	-2	6	1341	1319	-8	11	271	268	-4	14	432	419
-5	2	1070	1021	-2	7	512	456	-7	0	195	192	-4	15	135	123
-5	3	96	55	-2	8	696	679	-7	1	772	749	-3	0	1070	1073
-5	4	625	575	-2	9	124	136	-7	2	228	216	-3	1	268	283

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
H = 3**				-9	3	220	229	-4	11	191	193	-8	1	332	338
-3	2	636	617	-9	5	316	323	-4	13	267	271	-8	2	135	135
-3	3	426	423	-9	7	199	202	-4	14	345	333	-8	3	298	303
-3	4	1430	1359	-8	0	113	113	-4	15	95	95	-8	5	333	316
-3	5	776	740	-8	1	164	180	-3	0	1376	1310	-8	6	102	106
-3	6	474	464	-8	2	126	149	-3	1	1129	1118	-8	7	188	183
-3	7	182	202	-8	3	516	507	-3	2	547	566	-7	0	261	266
-3	8	918	860	-8	4	120	108	-3	3	143	141	-7	1	440	440
-3	9	391	358	-8	5	393	391	-3	4	976	955	-7	3	353	367
-3	10	160	152	-8	6	165	172	-3	5	496	453	-7	4	288	293
-3	11	272	263	-8	7	350	347	-3	6	193	197	-7	5	275	273
-3	12	691	643	-8	9	253	262	-3	7	279	285	-7	7	443	434
-3	13	201	210	-8	10	95	110	-3	8	741	724	-7	8	174	160
-3	15	254	248	-7	0	268	236	-3	9	162	144	-7	9	163	168
-3	16	375	361	-7	1	575	591	-3	11	291	309	-6	0	148	166
-2	0	1308	1316	-7	2	189	210	-3	12	495	493	-6	1	375	365
-2	1	97	104	-7	3	301	296	-3	15	150	162	-6	2	334	334
-2	2	1511	1505	-7	4	343	337	-2	0	876	884	-6	3	316	308
-2	3	507	455	-7	5	411	420	-2	1	506	462	-6	5	474	467
-2	4	728	744	-7	7	373	363	-2	2	1254	1284	-6	6	376	394
-2	5	467	397	-7	8	323	314	-2	3	474	473	-6	7	213	205
-2	6	1164	1186	-7	9	314	313	-2	4	437	402	-6	9	362	366
-2	7	221	252	-7	11	276	281	-2	5	260	240	-6	10	242	252
-2	8	402	395	-6	0	175	179	-2	6	1069	1046	-6	11	126	133
-2	9	316	297	-6	1	146	153	-2	7	207	208	-5	0	576	584
-2	10	901	893	-6	2	417	402	-2	9	281	262	-5	1	492	498
-2	11	195	202	-6	3	554	529	-2	10	795	774	-5	2	143	132
-2	12	121	61	-6	5	432	415	-2	12	113	116	-5	3	242	231
-2	13	226	226	-6	6	499	493	-2	13	221	209	-5	4	428	407
-2	14	612	594	-6	7	365	363	-2	14	480	476	-5	5	274	259
-2	17	124	126	-6	8	173	182	-2	16	89	118	-5	7	459	471
-1	0	1014	1029	-6	9	378	356	-1	0	1601	1497	-5	8	461	476
-1	1	325	297	-6	10	303	315	-1	1	325	336	-5	9	147	163
-1	2	1043	981	-6	11	210	190	-1	2	663	751	-5	11	322	321
-1	3	139	143	-6	13	245	253	-1	3	313	309	-5	12	269	272
-1	4	1728	1594	-5	0	434	429	-1	4	1228	1212	-4	0	206	207
-1	6	683	705	-5	1	733	689	-1	5	234	210	-4	1	395	400
-1	7	95	108	-5	2	176	181	-1	6	283	333	-4	2	659	647
-1	8	1234	1184	-5	3	179	171	-1	7	191	173	-4	3	526	542
-1	9	156	146	-5	4	638	624	-1	8	935	910	-4	5	344	341
-1	10	132	108	-5	5	563	529	-1	9	97	60	-4	6	708	682
-1	11	131	123	-5	7	223	217	-1	10	204	156	-4	7	217	219
-1	12	848	807	-5	8	543	512	-1	11	177	191	-4	8	114	113
-1	15	150	128	-5	9	257	248	-1	12	680	693	-4	9	268	280
-1	16	454	456	-5	11	337	334	-1	14	128	124	-4	10	448	441
0	0	1527	1558	-5	12	275	282	-1	16	324	337	-4	12	131	135
0	2	1025	991	-5	13	140	137	0	0	1017	1044	-4	13	203	230
0	4	906	925	-4	0	475	476	0	2	1323	1369	-3	0	1064	1092
0	6	938	993	-4	1	185	152	0	4	660	568	-3	1	351	332
0	8	436	406	-4	2	639	635	0	6	1325	1260	-3	2	113	140
0	10	1202	1186	-4	3	600	597	0	10	817	797	-3	3	395	368
0	14	677	691	-4	5	213	181	0	12	156	181	-3	4	779	780
0	16	88	68	-4	6	639	664	0	14	507	503	-3	5	374	354
H = 4**				-4	7	322	324	0	16	121	141	-3	6	116	95
-10	1	104	105	-4	8	151	148	**H = 5****				-3	7	266	265
-10	3	286	298	-4	9	361	339	-9	1	324	329	-3	8	612	642
-9	1	432	441	-4	10	581	549	-9	3	216	221	-3	9	105	80

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
H = 5**				-6	2	326	341	-1	7	154	140	-2	8	271	286
-3	10	142	152	-6	3	199	200	-1	8	586	605	-2	9	149	148
-3	11	246	246	-6	5	386	391	-1	10	220	239	-1	0	621	620
-3	12	407	413	-6	6	242	259	-1	12	319	334	-1	2	275	284
-2	0	130	97	-5	0	422	430	0	0	194	162	-1	3	102	95
-2	1	290	272	-5	1	201	203	0	2	953	931	-1	4	498	505
-2	2	1281	1241	-5	3	505	529	0	4	334	305	-1	6	291	318
-2	3	263	302	-5	4	433	464	0	6	611	639	-1	7	103	120
-2	5	336	365	-5	5	135	109	0	8	352	320	-1	8	316	332
-2	6	916	880	-5	7	394	409	0	10	446	485	0	0	240	252
-2	8	127	105	-5	8	281	288	0	12	209	201	0	2	436	473
-2	9	235	236	-4	1	287	302	**H = 7****				0	4	374	362
-2	10	605	588	-4	2	647	653	-7	0	136	133	0	6	356	390
-2	12	223	226	-4	3	113	126	-6	1	313	346	0	8	268	274
-2	13	105	117	-4	4	99	91	-6	2	243	251	**H = 8****			
-2	14	301	315	-4	5	335	374	-6	5	335	356	-5	0	186	203
-1	0	1303	1347	-4	6	445	439	-5	0	246	257	-5	2	101	119
-1	1	175	153	-4	8	247	244	-5	1	86	86	-4	0	151	152
-1	3	183	185	-4	9	296	308	-5	2	147	144	-4	1	253	244
-1	4	984	1063	-4	10	264	272	-5	3	336	333	-4	2	219	228
-1	6	190	167	-3	0	700	722	-5	4	307	342	-3	0	281	305
-1	7	244	216	-3	1	183	169	-5	6	129	137	-3	1	91	69
-1	8	764	776	-3	2	174	167	-4	0	102	126	-3	2	206	228
-1	10	185	174	-3	3	328	304	-4	1	255	285	-3	3	136	174
-1	11	107	83	-3	4	665	672	-4	2	348	360	-3	4	189	214
-1	12	457	486	-3	6	224	242	-4	3	131	97	-2	0	206	219
-1	14	165	186	-3	7	382	381	-4	4	241	243	-2	1	172	166
0	0	300	272	-3	8	489	511	-4	5	271	290	-2	2	301	299
0	2	1232	1153	-3	10	238	237	-4	6	302	329	-2	4	230	255
0	6	917	882	-3	11	136	139	-4	7	80	73	-2	5	132	117
0	8	145	140	-2	1	251	285	-3	0	512	541	-1	0	478	490
0	10	686	668	-2	2	819	831	-3	1	105	97	-1	2	275	299
0	12	249	233	-2	4	310	289	-3	2	210	210	-1	3	80	73
0	14	353	366	-2	5	238	241	-3	3	195	221	-1	4	258	255
H = 6**				-2	6	606	636	-3	4	434	446	-1	6	242	263
-8	1	285	296	-2	8	324	300	-3	6	244	248	0	0	248	290
-8	2	84	97	-2	9	195	196	-3	7	163	178	0	2	381	387
-8	3	171	167	-2	10	371	394	-3	8	207	215	0	4	259	258
-7	0	208	222	-2	12	207	221	-2	0	274	281	0	6	220	230
-7	1	267	261	-1	0	768	842	-2	2	511	533	**H = 9****			
-7	3	394	417	-1	2	300	316	-2	3	96	78	-2	0	209	223
-7	4	150	157	-1	3	191	159	-2	4	275	264	-1	0	183	192
-7	5	121	108	-1	4	670	682	-2	5	191	209	0	0	258	283
-6	1	438	458	-1	6	261	266	-2	6	317	323				

Table 28. 10*(Fobs vs. Fcal) for (PhCOCN2COPh).

K	L	FOBS	FCAL
H = 0**			
0	2	116	118
0	6	29	27
0	8	414	415
0	10	58	57
1	1	416	417
1	2	112	118
1	3	195	198
1	4	203	200
1	5	54	57
1	6	122	121
1	8	49	45
1	10	43	43
2	0	685	784
2	1	448	460
2	2	282	284
2	3	230	235
2	4	339	328
2	5	21	22
2	6	107	108
2	8	162	155
2	9	32	34
2	10	50	52
3	1	108	108
3	2	73	75
3	3	126	126
3	4	45	42
3	5	88	87
3	6	46	46
3	7	48	47
3	8	132	131
3	9	53	55
3	10	29	32
4	0	440	460
4	1	660	696
4	2	256	263
4	3	500	502
4	4	328	310
4	5	204	195
4	6	57	56
4	9	77	75
5	0	41	0
5	1	120	128
5	2	356	366
5	3	287	275
5	4	62	60
5	5	113	116
5	7	64	63
5	8	29	31
5	9	47	48
6	0	456	466
6	1	92	89
6	2	218	220
6	3	171	163
6	4	106	105
6	5	109	111
6	6	42	39
6	8	101	108
6	9	47	56
7	1	202	206
7	2	77	80
7	7	29	32
7	8	33	30
8	0	243	237
8	1	117	107
8	2	220	215
8	3	65	65
8	4	128	128
8	5	147	148
8	6	60	66
8	7	61	63
9	1	238	232
9	3	53	50
9	4	75	74
9	5	123	133
9	6	74	75
9	7	26	24
9	8	24	25
10	0	23	13
10	1	42	42
10	3	51	51
10	4	80	80
10	5	180	177
10	6	28	29
10	7	45	51
10	8	31	34
11	1	35	43
11	2	86	90
11	3	175	172
11	5	153	151
11	6	55	60
11	7	54	55
12	1	53	50
12	2	51	50
12	3	203	201
12	4	138	134
12	5	88	93
12	6	39	41
13	1	95	96
13	2	46	43
13	3	85	89
13	4	40	37
13	5	36	34
14	0	133	132
14	2	22	20
14	3	37	37
15	1	32	34
15	2	68	73
15	3	44	45
16	0	45	44
16	1	129	130
H = 1**			
0	-9	171	173
0	-7	229	231
0	-5	114	109
0	-3	262	268
0	-1	216	218
0	1	531	548
0	3	377	375
0	5	46	51
0	7	323	327
0	9	102	104
1	-10	24	21
1	-9	135	135
1	-8	83	83
1	-7	34	31
1	-6	33	33
1	-5	166	162
1	-4	52	49
1	-3	137	126
1	-2	283	283
1	-1	78	85
1	1	531	546
1	2	298	304
1	3	163	155
1	4	276	266
1	5	148	146
1	6	179	184
1	7	50	46
1	8	122	120
2	-10	41	43
2	-8	177	179
2	-7	47	45
2	-6	78	82
2	-5	197	193
2	-4	138	129
2	-2	99	95
2	-1	270	280
2	0	111	117
2	1	829	864
2	2	111	117
2	4	196	190
2	5	43	43
2	6	61	63
2	7	160	163
2	8	30	29
2	9	79	82
3	-10	62	64
3	-8	200	196
3	-7	70	75
3	-6	44	40
3	-5	147	138
3	-4	251	248
3	-3	131	123
3	-2	359	357
3	-1	527	570
3	0	596	641
3	1	444	459
3	2	636	646
3	3	74	65
3	4	105	101
3	5	140	139
3	6	130	136
3	7	40	39
3	8	64	62
3	9	65	58
4	-10	39	44
4	-9	66	62
4	-8	44	43
4	-7	165	167
4	-5	28	26
4	-4	182	181
4	-3	109	106
4	-2	70	71
4	-1	129	136
4	0	174	183
4	1	576	589
4	2	261	267
4	3	519	506
4	5	62	55
4	6	83	83
4	7	37	36
4	8	34	24
4	9	68	61
5	-9	43	37
5	-8	63	60
5	-6	110	105
5	-4	260	249
5	-3	176	181
5	-2	143	148
5	-1	299	320
5	0	41	7
5	1	203	212
5	2	139	134
5	3	26	21
5	4	106	106
5	5	223	221
5	6	64	67
5	7	28	33
5	8	51	50
5	9	48	44
6	-9	44	40
6	-6	85	82
6	-5	56	60
6	-4	41	39
6	-2	331	329
6	-1	141	138
6	0	239	233
6	1	170	173
6	2	340	339
6	4	81	78
6	5	52	51
6	6	49	44
6	7	142	146
7	-9	42	43
7	-8	46	48
7	-7	31	30
7	-5	112	107

Table 28. Continued

K	L	FOBS	FCAL
**H =	1****		
7	-3	48	44
7	-2	155	157
7	-1	53	55
7	0	24	32
7	1	183	183
7	2	44	48
7	4	162	165
7	5	51	53
7	6	88	93
7	7	36	34
7	8	35	37
8	-9	32	30
8	-8	38	43
8	-7	28	32
8	-6	49	50
8	-5	72	71
8	-4	121	121
8	-2	21	20
8	-1	120	115
8	0	63	59
8	1	64	66
8	2	165	162
8	4	52	55
8	5	58	59
8	7	73	74
9	-8	34	37
9	-7	33	39
9	-6	71	75
9	-5	67	73
9	-4	153	149
9	-2	360	348
9	-1	254	246
9	0	91	88
9	1	33	30
9	2	45	45
9	4	104	109
9	5	29	32
9	6	167	176
9	7	36	39
10	-8	41	45
10	-7	43	47
10	-6	27	20
10	-5	68	66
10	-4	64	61
10	-3	42	38
10	-2	98	96
10	-1	61	63
10	1	31	15
10	2	138	139
10	3	131	135
10	4	43	41
10	5	26	31
10	6	30	25
11	-6	74	80
11	-5	120	122
11	-3	90	89
11	0	41	39
11	1	81	80
11	2	160	160
11	3	53	57
11	4	139	140
11	7	21	27
12	-7	25	27
12	-6	27	21
12	-5	84	84
12	-4	84	86
12	-1	24	21
12	0	36	39
12	1	81	78
12	2	206	204
12	3	31	31
12	4	64	63
12	5	43	38
12	6	31	36
13	-6	24	26
13	-4	52	53
13	-3	60	59
13	-2	32	32
13	-1	22	25
13	0	52	52
13	1	192	187
13	3	68	65
13	4	70	72
13	5	46	44
14	-2	34	33
14	-1	47	43
14	0	62	58
14	2	50	50
14	3	31	37
15	-4	25	22
15	-2	44	42
15	0	56	59
15	3	34	36
16	1	27	27
**H =	2****		
0	-10	157	158
0	-8	36	32
0	-7	22	0
0	-6	191	188
0	-4	357	341
0	-2	1704	1801
0	0	244	251
0	2	280	274
0	4	101	94
0	6	61	62
0	8	66	67
1	-9	31	36
1	-7	88	86
1	-6	69	68
1	-5	86	86
1	-4	312	313
1	-3	215	214
1	-2	114	107
1	-1	488	537
1	0	150	141
1	1	133	140
1	2	351	355
1	3	110	101
1	4	87	80
1	5	164	168
1	6	99	96
2	-10	51	46
2	-9	220	219
2	-8	186	188
2	-7	91	89
2	-6	191	178
2	-5	387	378
2	-4	269	273
2	-3	515	535
2	-2	601	620
2	-1	826	890
2	0	510	525
2	1	83	87
2	2	366	358
2	3	72	72
2	4	46	40
2	5	195	195
2	6	183	184
2	7	29	33
3	-10	109	111
3	-9	53	56
3	-8	134	135
3	-7	150	152
3	-6	237	233
3	-5	109	109
3	-4	151	147
3	-3	92	95
3	-2	32	33
3	-1	433	462
3	0	550	571
3	1	210	204
3	2	263	263
3	3	151	141
3	4	104	105
3	5	74	68
3	6	134	135
3	7	44	41
3	8	90	92
4	-9	123	126
4	-7	101	103
4	-6	239	230
4	-5	141	141
4	-3	138	145
4	-2	36	32
4	-1	100	102
4	0	183	182
4	1	193	201
4	2	245	231
4	4	26	31
4	5	36	36
4	6	81	75
4	7	50	47
4	8	58	54
5	-10	73	76
5	-9	51	48
5	-8	70	70
5	-7	90	83
5	-5	34	40
5	-4	45	47
5	-3	366	372
5	-2	75	78
5	-1	381	389
5	0	39	42
5	1	269	271
5	2	50	44
5	3	171	170
5	4	41	41
5	6	52	53
5	7	76	79
5	8	37	34
6	-9	50	52
6	-8	83	85
6	-7	49	48
6	-6	71	70
6	-5	133	130
6	-4	337	335
6	-3	135	128
6	-2	241	234
6	-1	61	63
6	0	82	89
6	1	72	71
6	2	274	273
6	3	129	125
6	6	68	78
6	7	18	16
6	8	26	28
7	-8	58	62
7	-7	173	175
7	-5	72	68
7	-4	83	83
7	-3	21	22
7	-2	148	148
7	-1	39	40
7	0	298	297
7	1	261	272
7	2	22	18
7	4	62	63
7	6	24	29
7	7	36	36
8	-9	65	71
8	-8	43	37
8	-7	80	81
8	-6	127	134
8	-5	90	87
8	-3	144	137
8	-2	28	28
8	-1	218	208

K	L	FOBS	FCAL
**H =	2****		
8	0	106	111
8	1	71	76
8	2	111	112
8	4	91	91
8	5	28	31
8	6	74	76
8	7	41	51
9	-7	143	144
9	-6	176	172
9	-5	69	69
9	-4	138	142
9	-3	150	146
9	-2	46	46
9	-1	24	28
9	0	113	120
9	1	119	118
9	3	137	141
9	6	53	56
9	7	26	25
10	-7	136	135
10	-6	108	111
10	-4	58	63
10	-3	132	125
10	-2	36	38
10	-1	103	100
10	0	36	32
10	1	91	94
10	2	131	132
10	3	245	246
11	-7	101	100
11	-6	34	28
11	-5	77	77
11	-4	25	27
11	-3	54	49
11	-2	97	93
11	-1	73	67
11	1	178	173
11	2	25	16
11	3	121	122
11	5	29	27
12	-7	31	30
12	-5	121	120
12	-3	25	22
12	-2	77	75
12	-1	49	42
12	1	114	115
12	3	48	49
13	-7	50	48
13	-6	66	63
13	-5	97	99
13	-3	90	88
13	-1	149	149
13	1	55	54
13	3	42	43
14	-6	26	25
14	-5	42	42
14	-4	141	133
14	-3	35	32
14	-2	89	88
14	-1	22	18
14	0	53	48
14	1	21	11
14	3	23	21
15	-4	18	11
15	-3	97	97
15	-1	23	22
15	0	112	111
15	1	40	39
15	2	28	26
16	-1	87	88
**H =	3****		
0	-11	47	49
0	-9	290	291
0	-7	176	172
0	-5	50	53
0	-1	712	730
0	1	166	158
0	3	69	69
0	5	223	223
0	7	181	186
1	-10	108	106
1	-9	46	47
1	-8	138	138
1	-6	122	111
1	-5	61	56
1	-4	40	37
1	-3	522	527
1	-2	686	699
1	-1	46	46
1	0	347	342
1	1	115	118
1	2	237	230
1	3	260	255
1	4	112	107
1	5	64	57
1	6	23	19
1	7	30	29
1	8	67	68
2	-9	95	92
2	-8	77	75
2	-6	29	34
2	-5	145	137
2	-4	55	52
2	-3	72	74
2	-2	972	1026
2	-1	857	901
2	0	26	28
2	1	310	308
2	2	338	327
2	3	54	54
2	4	129	131
2	5	133	128
2	6	185	185
2	7	105	105
3	-10	44	46
3	-9	45	45
3	-8	24	27
3	-7	40	43
3	-6	131	133
3	-5	78	76
3	-4	63	62
3	-3	266	270
3	-2	205	212
3	0	404	411
3	1	26	30
3	3	44	46
3	5	33	35
3	7	18	8
4	-10	50	52
4	-9	112	115
4	-7	130	126
4	-6	202	200
4	-5	25	23
4	-4	26	20
4	-3	101	105
4	-2	470	484
4	-1	227	233
4	0	44	44
4	1	513	516
4	2	56	58
4	4	65	65
4	6	162	164
4	7	20	15
5	-10	67	65
5	-9	33	35
5	-8	141	143
5	-7	35	35
5	-6	25	20
5	-5	131	135
5	-4	140	140
5	-2	56	56
5	-1	282	281
5	0	295	302
5	1	149	146
5	2	110	112
5	3	23	25
5	4	108	109
5	5	27	27
5	6	65	67
5	7	52	56
6	-10	42	48
6	-8	43	41
6	-7	159	161
6	-6	63	61
6	-5	102	105
6	-4	204	197
6	-3	85	94
6	-2	273	257
6	-1	279	282
6	0	150	146
6	1	275	286
6	2	101	91
6	3	165	163
6	4	66	65
7	-9	47	46
7	-8	64	64
7	-6	25	24
7	-5	121	120
7	-4	34	36
7	-3	145	142
7	-2	43	42
7	-1	93	88
7	0	144	145
7	1	186	201
7	2	63	65
7	3	178	188
7	6	43	45
8	-9	31	35
8	-8	53	52
8	-7	118	119
8	-6	80	76
8	-5	85	90
8	-4	47	44
8	-3	26	32
8	-2	37	36
8	0	84	82
8	1	178	180
8	2	71	71
8	3	130	131
8	5	42	44
8	6	22	24
9	-9	20	18
9	-7	29	26
9	-6	72	72
9	-5	64	64
9	-4	87	86
9	-3	210	206
9	-2	78	76
9	0	35	37
9	1	164	164
9	2	213	218
9	3	104	110
9	4	38	40
9	5	34	32
9	6	22	22
10	-8	24	31
10	-6	143	141
10	-5	46	49
10	-4	80	74
10	-2	99	88
10	0	40	38
10	1	196	200
10	2	188	188
10	4	23	16
10	5	25	29
11	-6	30	32
11	-5	111	112

Table 28. Continued

K	L	FOBS	FCAL
**H =	3****		
11	-4	97	102
11	-3	98	91
11	-2	155	152
11	0	187	183
11	1	76	79
11	4	101	105
11	5	50	53
12	-7	78	77
12	-6	48	48
12	-5	35	30
12	-2	23	12
12	-1	72	73
12	0	138	133
12	1	48	50
12	2	58	62
12	3	73	72
12	4	56	56
13	-7	43	40
13	-5	47	52
13	-4	83	85
13	-3	41	41
13	-2	27	23
13	-1	35	43
13	0	24	24
13	1	148	139
13	2	39	34
13	4	65	61
14	-5	42	41
14	-3	18	15
14	-1	35	33
14	0	63	60
14	1	121	119
14	3	61	60
15	-4	41	40
15	-3	39	38
15	-1	23	27
15	0	45	38
15	1	48	54
**H =	4****		
0	-10	73	70
0	-8	29	22
0	-6	297	281
0	-4	225	225
0	-2	27	27
0	0	418	414
0	2	71	64
0	6	42	42
1	-11	56	56
1	-7	86	87
1	-6	161	154
1	-5	236	230
1	-4	92	87
1	-3	129	130
1	-2	87	86
1	-1	211	209
1	0	309	311
1	1	28	38
1	2	61	57
1	3	54	51
1	4	102	97
1	6	43	40
1	7	82	80
2	-11	65	65
2	-10	27	25
2	-6	101	97
2	-5	208	204
2	-4	379	374
2	-3	182	180
2	-2	170	176
2	-1	128	130
2	0	80	77
2	1	214	215
2	2	31	27
2	3	93	93
2	4	176	177
2	5	161	152
2	6	80	77
3	-10	87	84
3	-9	57	52
3	-7	57	61
3	-6	71	61
3	-5	50	48
3	-4	61	63
3	-3	158	163
3	-2	132	126
3	-1	50	51
3	1	114	111
3	2	27	32
3	3	71	70
3	4	62	66
3	5	49	44
3	7	33	33
4	-11	96	99
4	-10	21	18
4	-9	110	112
4	-8	136	133
4	-7	70	65
4	-6	103	103
4	-4	116	114
4	-3	107	100
4	-2	46	46
4	-1	185	185
4	0	294	285
4	1	78	74
4	2	25	26
4	3	141	135
4	4	68	69
4	5	32	34
5	-10	73	72
5	-9	44	42
5	-8	115	113
5	-6	24	22
5	-4	176	177
5	-3	251	249
5	-2	81	77
5	-1	204	199
5	1	77	80
5	2	111	110
5	3	146	148
5	4	148	149
5	5	77	77
5	6	34	33
6	-10	61	63
6	-8	118	121
6	-7	177	181
6	-6	63	38
6	-5	61	61
6	-4	49	45
6	-3	105	109
6	-2	226	217
6	-1	64	66
6	0	297	300
6	1	110	110
6	2	180	181
6	5	53	57
6	6	88	87
7	-9	32	28
7	-8	28	25
7	-7	25	3
7	-6	231	228
7	-5	83	86
7	-4	45	53
7	-3	30	23
7	-2	120	124
7	0	82	82
7	2	159	161
7	3	31	33
7	4	76	76
7	5	34	37
8	-10	32	32
8	-9	27	25
8	-8	130	130
8	-7	134	133
8	-6	137	141
8	-4	136	136
8	-3	130	120
8	-2	25	32
8	-1	30	25
8	0	47	48
8	1	54	56
8	2	239	250
8	3	103	104
8	4	69	75
8	6	17	15
9	-8	89	88
9	-7	147	150
9	-6	66	66
9	-3	130	126
9	1	117	122
9	2	63	61
9	3	35	38
9	4	53	53
9	5	41	42
10	-9	34	32
10	-8	56	58
10	-7	122	121
10	-6	71	70
10	-5	48	44
10	-2	59	60
10	-1	28	24
10	0	80	81
10	1	282	280
10	3	94	99
10	5	29	25
11	-8	25	21
11	-7	59	57
11	-6	47	46
11	-5	47	43
11	-4	35	31
11	-3	32	33
11	-2	61	66
11	-1	60	60
11	1	44	43
11	2	86	90
11	4	63	66
12	-7	93	92
12	-6	60	55
12	-3	23	19
12	-2	26	26
12	-1	104	106
12	0	41	41
12	1	67	66
12	2	73	74
12	3	51	49
13	-5	54	56
13	-4	41	41
13	-3	38	40
13	-1	19	18
14	-5	25	24
14	-3	46	46
14	-2	28	34
14	-1	25	25
14	1	40	40
15	-4	33	35
15	-2	56	58
15	-1	69	65
15	0	28	29
**H =	5****		
0	-11	26	24
0	-9	110	110
0	-7	173	166
0	-5	23	21
0	-3	133	133
0	-1	229	223
0	1	170	171
0	3	171	168
0	5	91	94

Table 28. Continued

K	L	FOBS	FCAL
H = 5**			
1	-11	26	24
1	-10	46	47
1	-9	75	77
1	-7	45	46
1	-6	110	107
1	-5	32	30
1	-4	420	414
1	-3	48	46
1	-2	97	90
1	-1	94	90
1	0	203	195
1	1	146	139
1	2	188	180
1	3	84	85
1	4	50	50
1	5	30	28
2	-10	77	75
2	-9	21	13
2	-8	80	81
2	-7	134	125
2	-6	29	31
2	-5	91	91
2	-4	508	506
2	-3	189	192
2	-1	108	106
2	0	29	24
2	1	84	85
2	2	67	66
2	3	156	148
2	4	173	173
2	5	30	26
3	-10	73	72
3	-9	138	139
3	-8	42	37
3	-6	71	75
3	-5	189	187
3	-4	37	36
3	-3	131	128
3	-2	102	102
3	-1	123	118
3	0	97	100
3	1	66	67
3	2	45	47
3	3	100	100
3	4	103	96
3	6	34	36
4	-11	33	30
4	-10	100	103
4	-8	97	95
4	-6	97	102
4	-5	44	35
4	-4	316	311
4	-3	278	289
4	-2	272	278
4	-1	130	130
4	0	187	189
4	1	58	60
4	3	54	56
4	4	191	187
4	5	86	88
5	-11	38	37
5	-10	36	41
5	-9	103	103
5	-8	23	23
5	-7	97	100
5	-6	89	86
5	-5	87	90
5	-4	35	36
5	-3	141	142
5	-2	43	30
5	-1	148	154
5	1	34	31
5	2	55	52
5	3	92	93
5	4	59	63
5	6	38	38
6	-10	35	36
6	-9	97	98
6	-8	115	115
6	-7	31	37
6	-6	117	115
6	-5	24	15
6	-4	48	44
6	-2	46	53
6	-1	27	29
6	0	162	154
6	1	123	121
6	2	93	95
6	4	27	25
6	5	31	32
7	-9	48	46
7	-8	94	91
7	-7	168	167
7	-6	134	131
7	-5	59	60
7	-4	104	102
7	-3	32	38
7	-2	49	48
7	-1	85	80
7	0	66	68
7	1	202	208
7	2	122	124
7	3	38	36
7	4	29	32
8	-9	22	23
8	-7	74	79
8	-6	105	111
8	-5	128	126
8	-3	96	95
8	-2	57	55
8	-1	70	74
8	0	94	92
8	1	25	23
8	2	36	38
9	-9	22	21
9	-8	89	86
9	-7	34	40
9	-5	33	32
9	-4	31	35
9	-3	73	69
9	-1	46	45
9	0	164	168
9	1	93	93
9	3	37	44
10	-9	28	25
10	-8	57	54
10	-6	55	53
10	-5	36	32
10	-4	41	39
10	-3	63	60
10	-1	98	98
10	0	65	71
10	1	24	15
10	3	37	40
11	-8	61	57
11	-7	39	42
11	-6	130	133
11	-4	60	62
11	-3	79	82
11	-2	66	65
11	-1	55	51
11	1	26	25
11	2	111	116
12	-7	43	46
12	-6	33	34
12	-5	80	81
12	-4	74	69
12	-3	47	48
12	-2	28	29
12	-1	56	52
12	0	75	76
12	1	22	20
12	2	62	59
13	-4	41	47
13	-2	31	34
13	-1	93	90
13	0	20	21
13	1	41	36
14	-4	47	45
14	-3	31	31
14	-1	47	48
14	0	19	9
H = 6**			
0	-10	30	36
0	-8	61	61
0	-6	68	70
0	-4	48	43
0	-2	281	269
0	0	252	246
0	4	28	22
1	-11	58	54
1	-10	18	9
1	-9	55	58
1	-8	41	43
1	-7	86	85
1	-6	55	55
1	-5	122	121
1	-4	212	213
1	-3	62	65
1	-1	171	166
1	0	93	93
1	2	57	56
1	3	27	26
2	-11	52	51
2	-9	45	46
2	-8	132	130
2	-7	41	38
2	-6	96	94
2	-5	233	233
2	-3	191	200
2	-2	34	37
2	-1	94	86
2	0	213	208
2	2	48	44
2	5	110	111
3	-11	21	18
3	-10	50	54
3	-8	40	45
3	-6	132	127
3	-5	47	50
3	-4	98	95
3	-3	90	97
3	-2	186	182
3	-1	137	136
3	0	39	32
3	1	23	17
3	2	79	71
3	3	41	43
3	4	30	25
4	-11	50	52
4	-10	38	39
4	-9	23	16
4	-7	43	44
4	-6	36	30
4	-5	64	61
4	-3	316	317
4	-2	122	123
4	-1	40	39
4	0	35	36
4	1	89	87
4	3	62	60
4	4	34	27
4	5	54	60
5	-10	47	43
5	-9	49	47
5	-7	63	68
5	-5	70	56

Table 28. Continued

K	L	FOBS	FCAL
H = 6**			
5	-4	88	84
5	-2	200	197
5	0	88	89
5	1	74	69
5	2	86	89
5	4	47	45
6	-10	19	18
6	-9	23	29
6	-8	48	49
6	-7	55	53
6	-6	50	52
6	-5	64	66
6	-4	69	66
6	-2	30	26
6	-1	128	120
6	0	77	77
6	1	46	45
6	2	61	57
6	3	57	62
6	4	28	34
7	-10	19	22
7	-8	144	146
7	-7	53	57
7	-6	96	96
7	-5	111	111
7	-3	25	17
7	-2	29	24
7	0	34	30
7	1	118	118
7	2	147	149
7	3	87	85
8	-9	63	65
8	-8	128	132
8	-7	53	53
8	-6	98	99
8	-5	48	45
8	-4	39	40
8	-3	54	55
8	-2	132	129
8	-1	36	38
8	0	167	167
8	1	76	77
8	2	56	61
8	3	19	4
9	-9	36	41
9	-7	158	159
9	-6	69	66
9	-3	27	24
9	1	96	102
9	2	25	23
10	-8	53	53
10	-5	97	98
10	-2	27	24
10	-1	29	32
11	-8	35	38
11	-6	31	26
11	-5	48	49
11	-4	22	18
11	-3	22	24
11	-2	31	29
11	-1	70	70
11	0	31	30
11	2	28	31
12	-7	35	32
12	-5	47	41
12	-4	32	36
12	-3	74	74
12	-2	86	84
12	0	26	28
12	1	67	63
13	-5	61	62
13	-4	27	24
13	-2	52	52
13	-1	25	22
H = 7**			
0	-9	55	61
0	-7	65	65
0	-1	106	102
0	1	50	51
0	3	126	124
1	-11	33	35
1	-10	60	63
1	-5	63	65
1	-4	46	41
1	-3	73	77
1	-2	161	156
1	-1	106	105
1	0	82	77
1	2	97	94
1	3	116	113
1	4	26	29
2	-11	45	46
2	-10	74	77
2	-8	74	68
2	-7	44	45
2	-6	134	130
2	-3	45	41
2	-2	59	56
2	1	30	24
2	2	131	128
3	-11	38	38
3	-9	58	56
3	-8	26	22
3	-7	25	20
3	-6	83	88
3	-5	112	113
3	-4	36	36
3	0	79	73
3	1	23	8
3	2	112	106
3	3	80	83
3	4	35	33
4	-10	27	26
4	-9	22	18
4	-8	33	35
4	-7	40	38
4	-6	275	277
4	-5	182	188
4	-2	28	31
4	-1	83	81
4	0	59	57
4	1	47	47
4	2	190	191
4	3	73	73
5	-10	29	32
5	-9	24	20
5	-8	37	33
5	-7	164	163
5	-6	106	105
5	-5	50	50
5	-3	51	49
5	-1	95	98
5	1	86	86
5	2	92	92
5	3	40	42
6	-10	78	77
6	-8	55	56
6	-7	49	50
6	-6	51	51
6	-5	72	73
6	-3	44	48
6	-2	106	108
6	-1	119	115
6	1	48	49
6	2	42	43
6	3	26	22
7	-9	34	33
7	-8	70	71
7	-7	54	49
7	-6	48	45
7	-5	30	31
7	-4	26	24
7	-3	92	93
7	-1	48	54
7	2	42	40
8	-9	45	46
8	-7	88	85
8	-4	23	20
8	-3	33	33
8	-2	144	143
8	-1	137	137
9	-5	51	52
9	-4	50	50
9	-3	56	55
9	-1	75	74
10	-8	21	21
10	-7	26	21
10	-6	40	40
10	-5	66	63
10	-4	46	56
10	-3	29	28
10	-1	59	58
10	1	44	41
11	-7	32	28
11	-6	24	18
11	-5	91	93
11	-3	24	26
12	-5	26	25
12	-4	21	21
12	-3	26	26
12	-1	34	34
H = 8**			
0	-6	77	76
0	-4	59	61
0	-2	102	101
1	-10	56	56
1	-9	63	65
1	-6	202	204
1	-5	24	24
1	-4	119	129
1	-3	74	71
1	-2	23	27
1	-1	46	48
1	0	28	34
1	1	37	34
1	2	25	28
2	-9	56	56
2	-7	87	91
2	-5	106	104
2	-3	53	55
2	-2	41	40
2	-1	77	75
2	1	59	62
3	-10	53	50
3	-9	35	36
3	-8	23	15
3	-7	31	29
3	-6	122	124
3	-5	165	163
3	-4	74	74
3	-3	42	39
3	0	63	66
4	-9	101	101
4	-8	26	24
4	-6	38	37
4	-5	61	60
4	-3	86	81
4	-1	68	69
4	1	61	62
4	2	33	30
5	-8	77	81
5	-7	42	42
5	-6	38	41
5	-4	35	29
5	-3	27	32
5	-2	23	8
5	-1	40	46

Table 28. Continued

K	L	FOBS	FCAL
H = 8**			
5	0	134	138
5	2	31	30
6	-9	23	18
6	-8	22	17
6	-7	45	51
6	-6	36	44
6	-4	43	48
6	-3	73	74
6	-2	32	38
6	1	72	73
7	-9	55	55
7	-8	55	54
7	-5	28	26
7	-3	36	38
7	-2	57	60
7	-1	65	68
7	0	76	81
7	1	26	23
8	-7	41	41
8	-5	26	32
8	-4	22	23
8	-3	47	49
9	-8	32	34
9	-7	29	28
9	-6	49	50
9	-4	54	60
9	-2	29	33
9	0	28	31
10	-7	44	49
10	-5	20	20
10	-4	26	19
10	-3	53	58
10	-2	26	28
10	-1	25	21
11	-4	22	21
11	-3	52	53
H = 9**			
0	-9	59	60
0	-7	46	38
0	-5	58	56
0	-3	59	54
0	1	18	11
1	-8	48	50
1	-7	53	51
1	-6	75	75
1	-5	45	50
1	-3	39	41
1	-2	60	60
1	1	61	56
2	-9	53	56
2	-8	46	45
2	-7	51	51
2	-6	65	61
2	-5	75	68
2	-4	120	121
2	-2	67	63
2	-1	61	58
2	0	64	62
3	-8	40	43
3	-7	91	90
3	-6	34	41
3	-5	46	52
3	-3	89	91
3	-2	54	51
3	0	22	25
4	-8	61	70
4	-7	58	61
4	-4	31	25
4	-2	67	70
4	0	37	37
5	-9	21	20
5	-8	24	22
5	-5	56	59
5	-3	38	38
5	-2	34	38
5	-1	50	51
5	0	24	27
6	-8	52	51
6	-7	61	63
6	-5	34	33
6	-4	65	65
6	-3	45	43
6	-2	77	76
6	-1	61	61
7	-8	58	57
7	-7	41	40
7	-5	29	28
7	-4	56	56
7	-3	40	42
8	-7	56	52
8	-6	29	27
8	-5	45	46
8	-4	77	78
8	-3	49	54
9	-6	22	26
9	-5	20	14
H = 10**			
0	-8	30	30
0	-4	42	42
0	-2	32	40
1	-8	19	19
1	-6	85	89
1	-5	63	67
1	-4	50	49
2	-8	28	27
2	-7	31	28
2	-5	33	35
2	-2	21	18
3	-8	31	33
3	-7	59	63
3	-6	68	67
3	-4	46	42
3	-3	59	59
3	-2	55	56
4	-7	47	44
4	-6	22	18
4	-5	51	55
4	-4	20	23
5	-7	60	61
5	-6	23	26
5	-3	45	48

Table 29. 10*(Fobs vs. Fcal) for (PhCOCN2Ph).

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
**H =	-6****			-3	-5	43	42	-7	-6	38	40	-2	-4	131	130
-5	-1	48	51	-3	-4	83	82	-7	-5	76	72	-2	-3	106	101
-4	-3	56	66	-3	-3	134	141	-7	-4	90	87	-2	-2	63	58
-4	-2	40	48	-3	-1	86	95	-7	-3	39	38	-2	-1	46	54
-4	-1	79	87	-2	-10	25	22	-7	-2	44	40	-2	0	72	75
-4	0	31	37	-2	-9	31	28	-7	-1	108	117	-1	-13	52	49
-3	-4	27	24	-2	-7	36	39	-7	0	117	118	-1	-11	27	29
-3	-3	36	41	-2	-5	87	90	-6	-11	33	36	-1	-10	36	42
-3	-2	38	30	-2	-4	117	127	-6	-10	45	48	-1	-9	28	32
-3	0	92	97	-2	-3	29	28	-6	-9	40	39	-1	-8	95	99
-2	-1	53	61	-2	-2	35	30	-6	-8	26	31	-1	-7	43	40
-2	0	39	60	-2	-1	91	92	-6	-6	98	94	-1	-6	216	213
-1	-4	38	28	-2	0	35	36	-6	-5	158	171	-1	-5	53	55
-1	-3	27	31	-1	-10	38	33	-6	-4	63	55	-1	-4	122	125
-1	-2	29	42	-1	-9	31	23	-6	-3	82	79	-1	-3	124	128
-1	-1	30	19	-1	-8	49	50	-6	-2	112	110	-1	-2	82	84
-1	0	35	31	-1	-7	48	56	-6	-1	81	82	-1	-1	81	86
0	-4	24	25	-1	-6	34	41	-6	0	38	32	-1	0	68	67
0	0	46	39	-1	-5	30	28	-5	-12	19	18	0	-13	29	45
**H =	-5****			-1	-4	39	39	-5	-11	30	36	0	-11	59	59
-9	-3	37	33	-1	-3	77	72	-5	-10	45	50	0	-10	120	106
-9	-2	39	44	-1	-2	82	80	-5	-9	29	28	0	-9	54	59
-9	-1	25	30	-1	0	81	79	-5	-8	78	79	0	-7	227	214
-8	-4	30	33	0	-5	31	23	-5	-7	25	23	0	-6	100	94
-8	-3	53	57	0	-4	119	124	-5	-6	47	50	0	-5	99	101
-7	-7	70	76	0	-1	26	38	-5	-4	32	33	0	-4	70	83
-7	-4	31	40	**H =	-4****			-5	-3	67	69	0	-3	52	45
-7	-3	38	40	-11	-5	21	21	-5	-2	83	80	0	0	53	56
-7	-2	37	41	-11	-2	44	42	-5	0	62	55	**H =	-3****		
-7	-1	29	26	-11	-1	38	31	-4	-12	24	25	-13	-1	48	49
-6	-8	78	79	-11	0	50	36	-4	-11	66	71	-12	-6	58	58
-6	-7	36	35	-10	-7	23	18	-4	-9	42	54	-12	-5	56	51
-6	-6	21	9	-10	-6	25	25	-4	-6	91	88	-12	-4	25	21
-6	-5	70	79	-10	-3	31	33	-4	-4	31	24	-12	-3	50	44
-6	-4	42	43	-10	-2	43	38	-4	-3	51	44	-12	-2	86	83
-6	-2	38	34	-10	-1	46	43	-4	-1	61	54	-12	-1	46	36
-6	-1	86	85	-10	0	38	35	-4	0	43	51	-12	0	62	53
-6	0	23	16	-9	-8	44	48	-3	-10	42	31	-11	-7	56	60
-5	-7	30	36	-9	-7	25	26	-3	-9	31	20	-11	-6	73	74
-5	-6	82	84	-9	-5	35	28	-3	-8	25	8	-11	-4	53	56
-5	-5	96	95	-9	-4	48	47	-3	-7	83	76	-11	-3	45	42
-5	-4	51	41	-9	-3	62	71	-3	-6	65	69	-11	-2	61	68
-5	-1	70	69	-9	-2	48	58	-3	-5	78	80	-11	-1	56	61
-5	0	52	47	-9	-1	42	41	-3	-4	60	67	-11	0	49	50
-4	-9	30	26	-9	0	71	72	-3	-3	60	60	-10	-10	33	42
-4	-8	33	25	-8	-9	26	24	-3	-2	125	122	-10	-9	36	31
-4	-7	65	69	-8	-7	39	41	-3	-1	101	103	-10	-7	65	71
-4	-6	25	31	-8	-6	77	76	-3	0	51	57	-10	-6	26	21
-4	-3	45	48	-8	-5	76	82	-2	-13	21	18	-10	-4	63	63
-4	-2	103	95	-8	-4	41	38	-2	-12	28	30	-10	-3	35	45
-4	-1	24	19	-8	-3	104	115	-2	-11	40	41	-10	-2	125	122
-4	0	38	33	-8	-2	61	55	-2	-10	55	55	-10	-1	32	39
-3	-10	29	21	-8	-1	84	88	-2	-9	34	32	-9	-11	23	32
-3	-9	26	24	-8	0	93	85	-2	-8	71	71	-9	-10	21	18
-3	-8	40	39	-7	-9	34	32	-2	-7	116	111	-9	-9	49	47
-3	-7	25	23	-7	-8	45	45	-2	-6	41	35	-9	-8	60	55
-3	-6	30	32	-7	-7	22	14	-2	-5	95	92	-9	-7	76	78

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
**H =		-3****		-4	-11	29	33	0	-13	59	55	-9	-4	28	18
-9	-6	63	77	-4	-10	77	83	0	-12	37	39	-9	-3	42	55
-9	-5	25	34	-4	-9	99	113	0	-10	176	164	-9	-2	176	180
-9	-4	108	101	-4	-8	96	100	0	-9	75	77	-9	-1	44	38
-9	-3	100	107	-4	-7	75	80	0	-8	71	70	-9	0	79	82
-9	-2	201	184	-4	-6	29	41	0	-6	27	34	-8	-13	23	23
-9	-1	72	68	-4	-5	93	81	0	-5	97	103	-8	-10	51	54
-9	0	67	64	-4	-4	104	108	0	-4	121	114	-8	-9	53	45
-8	-10	93	92	-4	-3	105	98	0	-3	61	53	-8	-8	97	100
-8	-9	26	27	-4	-2	93	89	0	-2	33	43	-8	-7	38	52
-8	-8	33	36	-4	-1	221	217	0	-1	23	27	-8	-6	76	80
-8	-7	53	46	-4	0	90	104	**H =		-2****		-8	-5	64	65
-8	-6	50	55	-3	-14	35	43	-14	-3	35	39	-8	-4	85	88
-8	-5	36	37	-3	-13	56	55	-14	-2	48	38	-8	-3	66	77
-8	-4	147	152	-3	-12	83	80	-14	-1	40	46	-8	-1	111	105
-8	-3	28	29	-3	-11	46	46	-14	0	26	23	-8	0	56	58
-8	-2	60	61	-3	-10	115	123	-13	-6	36	32	-7	-14	28	29
-8	-1	81	78	-3	-9	69	63	-13	-5	76	72	-7	-13	22	23
-8	0	210	218	-3	-8	72	73	-13	-4	60	65	-7	-12	75	75
-7	-10	45	53	-3	-7	117	116	-13	-3	29	29	-7	-11	35	34
-7	-9	49	44	-3	-6	95	101	-13	-2	32	29	-7	-10	54	49
-7	-8	41	41	-3	-5	146	144	-12	-8	28	25	-7	-9	61	61
-7	-7	25	26	-3	-4	83	88	-12	-6	79	78	-7	-8	63	62
-7	-5	90	88	-3	-2	183	173	-12	-5	47	57	-7	-7	44	49
-7	-4	56	57	-3	-1	58	63	-12	-4	57	57	-7	-6	36	37
-7	-3	91	90	-3	0	191	180	-12	-3	38	41	-7	-5	110	118
-7	-2	121	122	-2	-13	72	67	-12	-2	126	115	-7	-4	33	32
-7	-1	75	69	-2	-12	69	66	-12	-1	110	117	-7	-3	92	95
-6	-12	40	38	-2	-11	34	33	-11	-9	62	61	-7	-2	91	89
-6	-11	56	53	-2	-10	47	45	-11	-8	61	67	-7	-1	38	36
-6	-10	84	80	-2	-9	237	234	-11	-7	62	59	-7	0	58	52
-6	-9	27	32	-2	-8	171	166	-11	-6	71	73	-6	-14	48	47
-6	-8	79	88	-2	-7	111	117	-11	-5	39	41	-6	-13	57	53
-6	-7	55	51	-2	-6	62	58	-11	-4	67	68	-6	-12	59	59
-6	-6	97	93	-2	-5	89	95	-11	-3	125	120	-6	-11	66	71
-6	-5	55	69	-2	-4	87	73	-11	-2	113	112	-6	-10	28	29
-6	-4	101	101	-2	-3	141	146	-11	-1	95	90	-6	-9	25	16
-6	-3	56	56	-2	-2	193	201	-11	0	127	117	-6	-8	98	108
-6	-2	112	125	-2	-1	42	42	-10	-11	43	38	-6	-7	76	83
-6	-1	74	73	-1	-15	41	45	-10	-10	35	38	-6	-6	110	108
-6	0	136	138	-1	-14	65	62	-10	-9	50	53	-6	-5	45	45
-5	-14	37	33	-1	-13	66	68	-10	-7	50	58	-6	-4	162	159
-5	-13	39	40	-1	-12	43	42	-10	-6	130	131	-6	-3	35	30
-5	-12	64	59	-1	-11	39	40	-10	-5	29	31	-6	-2	95	95
-5	-10	37	42	-1	-10	83	78	-10	-4	133	129	-6	-1	56	56
-5	-9	28	25	-1	-9	176	168	-10	-3	46	36	-5	-15	32	35
-5	-8	51	60	-1	-8	66	70	-10	-2	72	69	-5	-14	47	46
-5	-7	92	86	-1	-7	81	80	-10	-1	80	76	-5	-12	63	68
-5	-6	76	83	-1	-6	106	100	-10	0	249	246	-5	-11	47	45
-5	-5	53	53	-1	-5	88	84	-9	-12	46	43	-5	-10	48	47
-5	-4	55	42	-1	-4	94	93	-9	-11	40	41	-5	-9	84	82
-5	-3	51	58	-1	-3	146	133	-9	-10	60	59	-5	-8	85	81
-5	-2	42	51	-1	-2	151	145	-9	-9	39	45	-5	-7	131	129
-5	-1	183	186	-1	-1	211	195	-9	-8	91	96	-5	-5	164	168
-5	0	54	75	-1	0	345	358	-9	-7	72	67	-5	-4	134	120
-4	-14	37	41	0	-15	21	10	-9	-6	118	118	-5	-3	200	189
-4	-12	40	33	0	-14	58	55	-9	-5	133	125	-5	-2	133	125

Table 29. Continued

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
H = -2**				-1	-8	35	37	-11	-3	88	80	-6	-12	81	86
-5	-1	148	140	-1	-7	87	79	-11	-2	70	65	-6	-11	77	79
-5	0	116	105	-1	-6	68	65	-11	-1	158	166	-6	-10	96	94
-4	-15	28	24	-1	-5	226	233	-10	-11	47	44	-6	-9	26	21
-4	-14	95	89	-1	-4	176	174	-10	-10	78	88	-6	-8	27	23
-4	-13	81	86	-1	-3	229	220	-10	-9	45	46	-6	-7	120	127
-4	-12	44	43	-1	-2	135	149	-10	-8	103	96	-6	-6	167	159
-4	-11	48	46	-1	-1	321	320	-10	-7	163	169	-6	-5	101	104
-4	-10	150	145	-1	0	400	412	-10	-6	82	82	-6	-4	144	136
-4	-9	129	133	0	-15	33	33	-10	-5	27	35	-6	-3	103	104
-4	-8	162	168	0	-14	88	98	-10	-4	152	146	-6	-2	121	121
-4	-7	67	76	0	-13	119	114	-10	-3	101	95	-6	-1	158	148
-4	-6	224	222	0	-12	26	27	-10	-2	62	60	-6	0	31	33
-4	-5	179	177	0	-11	58	57	-10	-1	33	35	-5	-14	101	96
-4	-4	265	265	0	-10	27	28	-10	0	139	137	-5	-13	47	47
-4	-3	229	230	0	-9	170	170	-9	-12	57	62	-5	-12	144	138
-4	-2	305	299	0	-8	108	111	-9	-10	117	115	-5	-11	88	83
-4	-1	54	50	0	-7	333	320	-9	-9	111	105	-5	-10	41	36
-4	0	70	67	0	-6	90	89	-9	-8	120	112	-5	-9	70	66
-3	-15	33	26	0	-5	196	212	-9	-7	51	55	-5	-8	73	65
-3	-14	110	102	0	-4	90	90	-9	-6	68	78	-5	-7	94	88
-3	-13	24	21	0	-3	91	92	-9	-5	87	92	-5	-5	211	194
-3	-12	58	46	0	-2	63	67	-9	-4	77	74	-5	-4	269	259
-3	-11	169	164	0	-1	328	350	-9	-3	123	127	-5	-3	59	65
-3	-10	108	106	0	0	344	348	-9	-2	82	83	-5	-2	95	91
-3	-9	113	110	**H = -1****				-9	-1	92	98	-5	-1	147	141
-3	-8	87	85	-15	-1	47	43	-8	-14	59	62	-4	-16	33	35
-3	-7	135	134	-14	-6	22	19	-8	-13	93	98	-4	-15	37	36
-3	-6	202	211	-14	-4	48	55	-8	-11	111	108	-4	-14	68	63
-3	-5	256	255	-14	-2	38	38	-8	-10	55	53	-4	-12	107	101
-3	-4	177	179	-14	-1	36	38	-8	-9	110	104	-4	-11	54	51
-3	-3	233	218	-13	-8	29	26	-8	-8	114	117	-4	-10	106	104
-3	-2	173	162	-13	-7	37	32	-8	-7	31	40	-4	-9	115	118
-3	-1	168	163	-13	-6	66	65	-8	-6	46	47	-4	-8	41	41
-3	0	21	24	-13	-5	30	24	-8	-5	101	100	-4	-7	56	54
-2	-16	44	41	-13	-4	79	83	-8	-4	37	36	-4	-6	267	256
-2	-15	53	51	-13	-3	58	53	-8	-3	95	96	-4	-5	195	196
-2	-14	23	16	-13	-1	58	56	-8	-2	95	91	-4	-4	246	249
-2	-13	83	78	-13	0	110	110	-8	-1	138	133	-4	-3	130	125
-2	-12	78	64	-12	-10	29	31	-8	0	50	48	-4	-2	140	138
-2	-11	125	116	-12	-9	39	39	-7	-14	63	63	-4	-1	260	255
-2	-10	35	30	-12	-8	35	37	-7	-13	62	62	-4	0	368	373
-2	-9	138	140	-12	-7	55	49	-7	-12	95	95	-3	-16	32	32
-2	-8	168	167	-12	-6	56	56	-7	-11	48	48	-3	-15	63	62
-2	-7	50	42	-12	-5	41	39	-7	-10	56	53	-3	-14	44	38
-2	-6	231	231	-12	-4	73	61	-7	-9	74	81	-3	-11	23	26
-2	-5	349	351	-12	-3	45	51	-7	-7	128	130	-3	-10	117	116
-2	-4	292	288	-12	-2	108	111	-7	-6	134	131	-3	-9	126	121
-2	-3	290	279	-12	-1	125	119	-7	-5	67	71	-3	-8	226	216
-2	-2	312	311	-11	-11	20	25	-7	-4	153	158	-3	-7	211	203
-2	-1	89	87	-11	-10	45	41	-7	-3	49	51	-3	-6	246	239
-2	0	162	164	-11	-9	30	27	-7	-2	56	53	-3	-5	186	188
-1	-15	23	19	-11	-8	35	38	-7	-1	171	165	-3	-4	447	449
-1	-14	48	46	-11	-7	64	58	-7	0	156	155	-3	-3	411	416
-1	-13	52	51	-11	-6	141	132	-6	-15	60	66	-3	-2	427	435
-1	-12	110	110	-11	-5	41	48	-6	-14	51	51	-3	-1	74	77
-1	-11	74	70	-11	-4	83	87	-6	-13	33	31	-3	0	168	177

Table 29. Continued

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
**H =		-1****		-14	0	29	32	-8	-3	54	51	-4	-4	202	208
-2	-16	41	44	-13	-8	27	17	-8	-2	66	58	-4	-3	92	98
-2	-15	37	38	-13	-7	65	62	-8	-1	65	56	-4	-2	287	290
-2	-14	75	71	-13	-6	50	46	-8	0	133	126	-4	-1	36	49
-2	-13	63	60	-13	-5	30	23	-7	-15	29	28	-4	0	81	81
-2	-12	44	43	-13	-4	94	92	-7	-14	55	51	-3	-15	48	49
-2	-11	73	72	-13	-3	104	108	-7	-12	29	29	-3	-14	38	39
-2	-10	74	73	-13	-2	57	58	-7	-11	212	212	-3	-13	38	38
-2	-9	101	98	-13	-1	110	110	-7	-10	122	124	-3	-12	106	100
-2	-8	149	155	-12	-10	35	33	-7	-9	69	69	-3	-11	92	93
-2	-7	111	107	-12	-9	49	54	-7	-8	105	118	-3	-10	164	153
-2	-6	231	230	-12	-8	78	72	-7	-7	82	90	-3	-9	90	86
-2	-5	413	413	-12	-7	30	21	-7	-5	162	159	-3	-8	81	78
-2	-4	197	208	-12	-6	93	97	-7	-4	158	172	-3	-7	34	35
-2	-3	302	311	-12	-5	112	120	-7	-3	245	230	-3	-6	123	116
-2	-2	820	860	-12	-4	28	33	-7	-2	190	193	-3	-5	20	20
-2	-1	634	659	-12	-3	26	6	-7	-1	249	238	-3	-4	67	66
-2	0	391	417	-12	-1	55	47	-6	-14	21	16	-3	-3	41	41
-1	-15	29	36	-12	0	130	116	-6	-13	110	112	-3	-2	72	76
-1	-12	51	46	-11	-11	32	24	-6	-12	65	72	-3	-1	98	97
-1	-11	22	17	-11	-10	87	86	-6	-10	136	136	-2	-14	48	50
-1	-10	70	67	-11	-8	33	42	-6	-9	58	50	-2	-11	27	22
-1	-9	152	153	-11	-7	78	84	-6	-8	227	232	-2	-10	28	24
-1	-8	103	99	-11	-6	71	63	-6	-7	146	142	-2	-9	101	96
-1	-7	273	266	-11	-5	116	117	-6	-6	143	128	-2	-8	193	189
-1	-6	156	154	-11	-3	88	89	-6	-5	166	171	-2	-7	93	97
-1	-5	209	209	-11	-2	86	92	-6	-3	88	87	-2	-6	82	82
-1	-4	444	456	-11	-1	65	60	-6	-2	332	321	-2	-5	26	28
-1	-3	146	149	-10	-10	81	79	-6	-1	221	221	-2	-4	522	530
-1	-2	385	405	-10	-8	48	57	-6	0	101	95	-2	-3	222	222
-1	-1	339	351	-10	-7	51	43	-5	-16	68	69	-2	-2	577	596
-1	0	24	23	-10	-6	25	23	-5	-15	55	51	-2	-1	496	526
0	-16	65	63	-10	-5	105	103	-5	-14	56	59	-2	0	507	519
0	-15	33	35	-10	-3	73	72	-5	-11	179	178	-1	-13	83	76
0	-13	23	5	-10	-2	76	92	-5	-10	117	107	-1	-12	95	92
0	-12	66	60	-9	-12	93	92	-5	-8	24	17	-1	-11	34	23
0	-11	77	77	-9	-11	29	30	-5	-7	123	128	-1	-10	62	54
0	-10	89	94	-9	-9	68	75	-5	-6	177	173	-1	-9	54	52
0	-9	159	161	-9	-8	84	89	-5	-5	106	109	-1	-8	332	312
0	-8	136	132	-9	-7	110	118	-5	-4	112	116	-1	-7	47	45
0	-7	309	309	-9	-6	40	40	-5	-3	112	103	-1	-6	226	232
0	-6	71	75	-9	-5	143	137	-5	-2	125	117	-1	-5	255	267
0	-5	319	325	-9	-4	35	41	-5	-1	230	223	-1	-4	601	616
0	-4	826	846	-9	-3	95	94	-4	-16	35	29	-1	-3	129	127
0	-3	990	1043	-9	-2	83	87	-4	-15	59	57	-1	-2	372	381
0	-2	306	308	-9	-1	33	27	-4	-13	86	86	-1	-1	216	227
0	-1	43	41	-8	-12	110	114	-4	-12	39	42	0	-16	53	56
**H =		0****		-8	-11	33	35	-4	-11	23	27	0	-12	86	81
-15	-2	19	16	-8	-10	116	122	-4	-9	76	86	0	-10	34	29
-15	-1	33	39	-8	-9	227	223	-4	-8	38	32	0	-8	58	53
-14	-5	29	28	-8	-8	204	206	-4	-7	140	134	0	-6	191	196
-14	-4	96	98	-8	-7	128	126	-4	-6	90	82	0	-4	992	1043
-14	-2	26	28	-8	-5	123	119	-4	-5	225	230	0	-2	268	281
-14	-1	28	32	-8	-4	149	134								

Table 30. 10*(Fobs vs. Fcal) for [IrCl((C6H4)COCC(Ph)OPPh2)(PPh3)2]. 176

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
H = 0**				-7	-4	278	276	-5	8	309	319	-2	-8	277	265
-11	1	225	237	-7	-3	425	411	-5	9	265	269	-2	-7	330	335
-11	2	303	291	-7	-2	632	635	-5	10	252	244	-2	-6	436	425
-11	3	237	227	-7	-1	531	537	-5	11	195	194	-2	-5	451	439
-11	4	175	166	-7	0	459	424	-5	12	171	173	-2	-4	711	683
-11	5	133	128	-7	1	422	422	-4	-10	157	167	-2	-3	765	761
-11	6	144	140	-7	2	558	560	-4	-9	203	201	-2	-2	909	888
-10	-3	276	277	-7	3	557	551	-4	-8	187	196	-2	-1	499	501
-10	-2	287	295	-7	4	510	499	-4	-7	253	240	-2	0	862	883
-10	-1	290	272	-7	5	110	121	-4	-6	388	373	-2	1	350	349
-10	0	285	288	-7	6	76	81	-4	-5	310	325	-2	2	715	745
-10	1	381	363	-7	7	163	163	-4	-4	399	390	-2	3	872	882
-10	2	257	252	-7	8	202	198	-4	-3	507	510	-2	4	758	770
-10	3	253	253	-7	9	177	181	-4	-2	940	911	-2	5	513	490
-10	4	195	203	-7	10	256	255	-4	-1	874	894	-2	6	406	433
-10	5	253	243	-7	11	180	175	-4	0	660	664	-2	7	351	348
-10	6	148	158	-7	12	135	139	-4	1	767	779	-2	8	424	440
-10	7	168	166	-6	-9	249	251	-4	2	320	328	-2	9	373	365
-10	8	194	195	-6	-8	231	238	-4	3	506	524	-2	10	298	302
-9	-5	176	181	-6	-7	350	344	-4	4	896	901	-2	11	314	311
-9	-4	206	206	-6	-6	377	386	-4	5	716	732	-2	12	237	247
-9	-3	310	313	-6	-5	339	355	-4	6	381	397	-2	13	163	166
-9	-2	491	494	-6	-4	399	389	-4	7	345	336	-1	-12	230	241
-9	-1	391	394	-6	-3	393	392	-4	8	292	297	-1	-11	322	331
-9	0	403	391	-6	-2	509	539	-4	9	202	194	-1	-10	285	284
-9	1	250	261	-6	-1	561	586	-4	10	300	295	-1	-9	357	347
-9	2	294	277	-6	0	483	486	-4	11	245	254	-1	-8	261	272
-9	3	297	298	-6	1	526	538	-4	12	248	247	-1	-7	324	307
-9	4	285	273	-6	2	517	506	-4	13	157	153	-1	-6	509	524
-9	5	279	273	-6	3	558	551	-3	-11	188	190	-1	-5	949	930
-9	6	305	289	-6	4	394	402	-3	-10	216	226	-1	-4	783	780
-9	7	208	181	-6	5	324	323	-3	-9	252	243	-1	-3	543	513
-9	8	192	198	-6	6	199	202	-3	-8	284	306	-1	-2	377	334
-9	9	231	241	-6	7	250	253	-3	-7	459	450	-1	-1	1094	1108
-9	10	239	235	-6	8	279	267	-3	-6	396	389	-1	0	1182	1439
-8	-6	177	197	-6	9	309	322	-3	-5	516	498	-1	1	1184	1361
-8	-5	196	188	-6	10	228	236	-3	-4	356	364	-1	2	484	483
-8	-4	194	197	-6	11	134	127	-3	-3	802	786	-1	3	919	942
-8	-3	328	329	-6	12	147	147	-3	-2	741	755	-1	4	610	591
-8	-2	470	491	-5	-10	231	236	-3	-1	878	853	-1	5	352	346
-8	-1	478	465	-5	-9	221	230	-3	0	762	777	-1	6	302	300
-8	0	174	174	-5	-8	209	205	-3	1	627	658	-1	7	418	402
-8	1	255	257	-5	-7	307	301	-3	2	544	555	-1	8	295	297
-8	2	419	416	-5	-6	392	406	-3	3	719	745	-1	9	203	186
-8	3	592	588	-5	-5	391	375	-3	4	820	844	-1	10	190	184
-8	4	374	367	-5	-4	255	260	-3	5	654	670	-1	11	295	286
-8	5	230	249	-5	-3	349	336	-3	6	176	171	-1	12	247	243
-8	6	214	192	-5	-2	643	651	-3	7	288	302	0	-12	308	300
-8	7	151	150	-5	-1	599	631	-3	8	196	188	0	-11	256	262
-8	8	193	207	-5	0	649	642	-3	9	218	230	0	-10	255	269
-8	9	212	226	-5	1	781	788	-3	10	261	266	0	-9	234	226
-8	10	226	215	-5	2	522	528	-3	11	256	243	0	-8	261	272
-8	11	212	205	-5	3	451	470	-3	12	261	255	0	-7	452	461
-7	-8	272	280	-5	4	493	496	-3	13	181	191	0	-6	586	587
-7	-7	220	225	-5	5	418	435	-2	-11	242	251	0	-5	595	606
-7	-6	280	278	-5	6	316	310	-2	-10	328	326	0	-4	675	690
-7	-5	297	306	-5	7	285	306	-2	-9	233	241	0	-3	672	672

Table 30. Continued

K	L	FOBS	FCAL
H = 0**			
0	-2	490	470
0	-1	1263	1470
0	1	1217	1433
0	2	553	529
0	3	669	668
0	4	632	647
0	5	547	556
0	6	520	523
0	7	433	431
0	8	200	205
0	9	189	182
0	10	223	231
0	11	232	231
0	12	291	274
1	-12	257	265
1	-11	309	300
1	-10	163	154
1	-9	226	215
1	-8	308	309
1	-7	443	425
1	-6	335	340
1	-5	397	391
1	-4	626	610
1	-3	895	918
1	-2	491	486
1	-1	1188	1365
1	0	1151	1411
1	1	1089	1104
1	2	472	430
1	3	568	538
1	4	821	822
1	5	988	969
1	6	501	523
1	7	312	292
1	8	248	251
1	9	316	309
1	10	300	297
1	11	314	325
1	12	232	226
2	-13	176	177
2	-12	258	265
2	-11	313	313
2	-10	276	287
2	-9	381	371
2	-8	424	444
2	-7	370	372
2	-6	426	454
2	-5	425	411
2	-4	772	781
2	-3	844	856
2	-2	701	727
2	-1	264	267
2	0	817	847
2	1	510	504
2	2	876	857
2	3	771	768
2	4	684	656
2	5	484	484
2	6	465	448
2	7	325	318
2	8	224	215
2	9	233	233
2	10	337	327
2	11	261	260
3	-13	191	198
3	-12	242	249
3	-11	259	254
3	-10	293	294
3	-9	220	231
3	-8	202	193
3	-7	329	343
3	-6	191	180
3	-5	633	656
3	-4	818	841
3	-3	734	755
3	-2	543	555
3	-1	636	666
3	0	756	779
3	1	843	812
3	2	763	773
3	3	793	782
3	4	361	371
3	5	550	533
3	6	419	411
3	7	422	412
3	8	253	266
3	9	234	228
3	10	229	225
3	11	182	183
4	-13	171	169
4	-12	236	244
4	-11	266	275
4	-10	340	342
4	-9	240	237
4	-8	298	299
4	-7	314	307
4	-6	421	434
4	-5	710	731
4	-4	858	869
4	-3	493	518
4	-2	328	337
4	-1	755	775
4	0	613	626
4	1	858	890
4	2	913	892
4	3	525	518
4	4	416	403
4	5	336	343
4	6	391	368
4	7	194	182
4	8	165	172
4	9	220	210
4	10	172	170
5	-12	193	190
5	-11	190	202
5	-10	265	263
5	-9	265	273
5	-8	300	305
5	-7	295	330
5	-6	364	359
5	-5	455	474
5	-4	466	476
5	-3	410	429
5	-2	543	544
5	-1	764	782
5	0	658	649
5	1	630	659
5	2	641	651
5	3	356	342
5	4	249	254
5	5	394	374
5	6	418	433
5	7	335	324
5	8	212	206
5	9	220	228
5	10	213	221
6	-12	161	157
6	-11	155	151
6	-10	243	254
6	-9	300	316
6	-8	276	269
6	-7	279	289
6	-6	208	208
6	-5	333	339
6	-4	360	379
6	-3	555	551
6	-2	498	501
6	-1	542	544
6	0	508	519
6	1	573	606
6	2	523	561
6	3	389	386
6	4	398	393
6	5	334	349
6	6	402	410
6	7	365	356
6	8	214	214
6	9	228	226
7	-12	150	148
7	-11	187	190
7	-10	256	270
7	-9	191	189
7	-8	223	226
7	-7	173	168
7	-5	174	178
7	-4	511	504
7	-3	547	541
7	-2	571	570
7	-1	423	428
7	0	479	447
7	1	561	563
7	2	655	658
7	3	435	419
7	4	293	293
7	5	319	336
7	6	283	282
7	7	224	229
7	8	253	262
8	-11	224	216
8	-10	216	216
8	-9	236	255
8	-8	192	211
8	-7	168	159
8	-6	181	166
8	-5	226	243
8	-4	360	347
8	-3	565	554
8	-2	398	399
8	-1	254	244
8	0	225	216
8	1	490	476
8	2	485	515
8	3	347	354
8	4	217	224
8	5	213	207
8	6	188	202
9	-10	251	249
9	-9	232	242
9	-8	191	200
9	-7	199	178
9	-6	305	295
9	-5	279	280
9	-4	311	298
9	-3	303	299
9	-2	272	260
9	-1	259	273
9	0	391	375
9	1	378	383
9	2	488	500
9	3	318	320
9	4	208	201
9	5	156	166
10	-8	203	195
10	-7	164	166
10	-6	167	173
10	-5	273	264
10	-4	203	216
10	-3	232	235
10	-2	253	259
10	-1	379	362
10	0	276	276
10	1	296	281
10	2	306	311
10	3	283	283
11	-6	138	136
11	-5	121	122
11	-4	164	154

Table 30. Continued

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
**H =		0****		-8	11	147	147	-5	4	609	625	-2	-12	208	215
11	-3	238	223	-7	-8	277	269	-5	5	435	442	-2	-11	293	301
11	-2	294	289	-7	-7	182	193	-5	6	475	482	-2	-10	302	298
11	-1	235	245	-7	-6	174	167	-5	7	347	341	-2	-9	236	241
**H =		1****		-7	-5	168	165	-5	8	337	336	-2	-8	416	403
-11	0	242	236	-7	-4	294	311	-5	9	352	363	-2	-7	376	368
-11	1	272	283	-7	-3	511	521	-5	10	349	355	-2	-6	495	473
-11	2	355	355	-7	-2	440	431	-5	11	244	251	-2	-5	512	483
-11	3	323	326	-7	-1	423	412	-5	12	150	158	-2	-4	770	747
-11	4	251	250	-7	0	412	414	-4	-10	174	179	-2	-3	644	630
-11	5	212	214	-7	1	477	468	-4	-9	228	216	-2	-2	366	373
-11	6	220	204	-7	2	679	663	-4	-8	268	261	-2	-1	932	901
-10	-3	231	221	-7	3	755	768	-4	-7	370	354	-2	0	483	487
-10	-2	237	234	-7	4	610	609	-4	-6	384	381	-2	1	587	594
-10	-1	241	238	-7	5	405	405	-4	-5	285	281	-2	2	1107	1158
-10	0	322	320	-7	6	280	276	-4	-4	203	192	-2	3	402	432
-10	1	463	447	-7	7	201	201	-4	-3	290	303	-2	4	584	588
-10	2	383	370	-7	8	277	272	-4	-2	924	912	-2	5	715	715
-10	3	385	375	-7	9	326	327	-4	-1	983	973	-2	6	441	439
-10	4	355	343	-7	10	252	243	-4	0	641	651	-2	7	415	418
-10	5	281	272	-7	11	134	146	-4	1	556	574	-2	8	429	422
-10	6	237	238	-6	-9	180	181	-4	2	475	479	-2	9	410	408
-10	7	282	274	-6	-8	193	194	-4	3	521	549	-2	10	309	302
-10	8	276	281	-6	-7	303	311	-4	4	693	691	-2	11	255	261
-9	-5	175	183	-6	-6	261	278	-4	5	844	873	-2	12	121	126
-9	-4	226	214	-6	-5	228	220	-4	6	423	430	-2	13	130	125
-9	-3	251	249	-6	-4	415	412	-4	7	500	492	-1	-12	227	224
-9	-2	330	340	-6	-3	484	514	-4	8	385	410	-1	-11	279	272
-9	-1	367	368	-6	-2	427	404	-4	9	246	260	-1	-10	166	165
-9	0	364	358	-6	-1	308	306	-4	10	386	375	-1	-9	351	332
-9	1	252	271	-6	0	510	499	-4	11	283	271	-1	-8	373	384
-9	2	273	254	-6	1	551	557	-4	12	152	171	-1	-7	406	396
-9	3	298	291	-6	2	678	698	-3	-11	206	195	-1	-6	463	463
-9	4	264	278	-6	3	646	646	-3	-10	251	260	-1	-5	714	684
-9	5	315	307	-6	4	441	462	-3	-9	314	313	-1	-4	688	674
-9	6	390	395	-6	5	527	549	-3	-8	359	354	-1	-3	491	482
-9	7	287	288	-6	6	425	411	-3	-7	459	454	-1	-2	1322	1338
-9	8	284	261	-6	7	272	289	-3	-6	382	367	-1	-1	793	812
-9	9	253	251	-6	8	286	312	-3	-5	323	309	-1	0	978	1033
-9	10	137	127	-6	9	344	330	-3	-4	424	408	-1	1	628	659
-8	-6	206	211	-6	10	261	271	-3	-3	677	657	-1	2	863	898
-8	-5	255	230	-6	11	139	130	-3	-2	835	813	-1	3	1012	1013
-8	-4	281	279	-6	12	123	131	-3	-1	718	731	-1	4	828	848
-8	-3	325	331	-5	-10	163	164	-3	0	771	777	-1	5	856	856
-8	-2	411	400	-5	-9	158	153	-3	1	647	658	-1	6	615	631
-8	-1	411	427	-5	-8	179	175	-3	2	542	569	-1	7	529	513
-8	0	212	225	-5	-7	307	326	-3	3	774	788	-1	8	356	376
-8	1	254	250	-5	-6	458	470	-3	4	1007	1053	-1	9	269	264
-8	2	383	368	-5	-5	252	240	-3	5	845	854	-1	10	337	298
-8	3	515	506	-5	-4	389	382	-3	6	485	505	-1	11	155	160
-8	4	516	486	-5	-3	398	415	-3	7	357	348	-1	12	218	201
-8	5	346	347	-5	-2	426	420	-3	8	362	354	0	-12	268	251
-8	6	321	336	-5	-1	667	667	-3	9	235	223	0	-11	259	248
-8	7	197	164	-5	0	553	577	-3	10	309	308	0	-10	270	273
-8	8	210	200	-5	1	894	886	-3	11	241	245	0	-9	299	298
-8	9	209	199	-5	2	728	729	-3	12	148	144	0	-8	317	300
-8	10	179	191	-5	3	493	510	-3	13	150	143	0	-7	357	349

Table 30. Continued

K	L	FOBS	FCAL
H = 1**			
0	-6	279	264
0	-5	431	432
0	-4	549	522
0	-3	137	124
0	-2	384	369
0	-1	872	881
0	0	1166	1376
0	1	760	734
0	2	719	738
0	3	1104	1116
0	4	660	678
0	5	678	679
0	6	559	570
0	7	577	589
0	8	371	369
0	9	372	360
0	10	298	276
0	11	302	315
0	12	285	297
1	-13	207	211
1	-12	268	280
1	-11	374	369
1	-10	337	344
1	-9	281	268
1	-8	401	407
1	-7	453	443
1	-6	512	515
1	-5	654	655
1	-4	960	1007
1	-3	851	876
1	-2	516	526
1	-1	473	476
1	0	933	946
1	1	759	773
1	2	200	175
1	3	419	390
1	4	564	551
1	5	670	668
1	6	549	526
1	7	343	341
1	8	348	336
1	9	241	235
1	10	380	355
1	11	289	306
1	12	227	229
2	-13	212	201
2	-12	225	233
2	-11	325	317
2	-10	358	359
2	-9	280	279
2	-8	368	371
2	-7	293	316
2	-6	401	391
2	-5	391	411
2	-4	415	403
2	-3	254	270
2	-2	775	790
2	-1	1043	1126
2	0	607	608
2	1	646	631
2	2	753	742
2	3	793	783
2	4	527	535
2	5	785	771
2	6	568	567
2	7	382	368
2	8	281	275
2	9	326	331
2	10	312	309
2	11	228	233
3	-13	222	231
3	-12	288	298
3	-11	211	218
3	-10	253	245
3	-9	276	274
3	-8	241	246
3	-7	240	242
3	-6	368	382
3	-5	541	543
3	-4	514	521
3	-3	483	492
3	-2	441	467
3	-1	510	500
3	0	642	641
3	1	914	926
3	2	827	813
3	3	554	554
3	4	593	563
3	5	518	517
3	6	546	532
3	7	426	418
3	8	343	339
3	9	282	283
3	10	202	203
3	11	156	166
4	-13	207	208
4	-12	284	266
4	-11	268	264
4	-10	312	313
4	-9	259	263
4	-8	235	228
4	-7	213	236
4	-6	267	251
4	-5	539	546
4	-4	484	497
4	-3	335	347
4	-2	351	336
4	-1	392	376
4	0	740	754
4	1	1017	1026
4	2	836	826
4	3	486	480
4	4	430	429
4	5	537	535
4	6	563	565
4	7	349	338
4	8	297	298
4	9	235	237
4	10	167	161
5	-12	254	240
5	-11	294	306
5	-10	332	338
5	-9	328	320
5	-8	273	262
5	-7	237	229
5	-6	237	250
5	-5	288	304
5	-4	245	234
5	-3	224	221
5	-2	374	378
5	-1	466	473
5	0	520	538
5	1	499	517
5	2	518	514
5	3	312	318
5	4	449	455
5	5	622	604
5	6	533	541
5	7	415	418
5	8	216	208
5	9	198	200
6	-12	206	218
6	-11	220	225
6	-10	303	301
6	-9	351	349
6	-8	252	251
6	-7	323	329
6	-6	296	294
6	-5	258	232
6	-4	314	308
6	-3	484	478
6	-2	416	394
6	-1	384	377
6	0	447	451
6	1	362	366
6	2	459	467
6	3	442	434
6	4	521	531
6	5	485	471
6	6	355	347
6	7	305	312
6	8	206	209
7	-12	209	204
7	-11	277	272
7	-10	311	313
7	-9	218	227
7	-8	240	232
7	-7	228	232
7	-6	83	82
7	-5	215	198
7	-4	537	532
7	-3	488	510
7	-2	301	307
7	-1	207	204
7	0	302	315
7	1	495	502
7	2	542	530
7	3	358	349
7	4	325	339
7	5	249	260
7	6	161	171
7	7	248	247
8	-11	280	279
8	-10	250	255
8	-9	292	272
8	-8	194	198
8	-7	257	251
8	-6	243	221
8	-5	153	171
8	-4	341	334
8	-3	481	454
8	-2	346	342
8	-1	214	208
8	0	394	394
8	1	519	514
8	2	351	367
8	3	275	278
8	4	203	217
8	5	166	165
8	6	234	213
9	-10	232	234
9	-9	204	195
9	-8	224	229
9	-7	202	214
9	-6	197	179
9	-5	211	207
9	-4	149	142
9	-3	239	223
9	-2	265	267
9	-1	263	240
9	0	341	352
9	1	353	364
9	2	361	358
9	3	242	243
9	4	198	199
10	-8	229	231
10	-7	158	151
10	-6	136	130
10	-5	211	200
10	-4	170	162
10	-3	182	197
10	-2	239	248
10	-1	243	243
10	0	221	219
10	1	225	217
10	2	229	225
11	-5	81	94

Table 30. Continued

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
H = 1**				-8	10	267	268	-5	3	435	462	-2	-12	268	267
11	-4	154	160	-8	11	166	159	-5	4	452	462	-2	-11	298	305
11	-3	214	206	-7	-8	216	236	-5	5	556	578	-2	-10	273	267
11	-2	233	232	-7	-7	170	164	-5	6	521	541	-2	-9	266	266
11	-1	175	175	-7	-6	126	124	-5	7	463	483	-2	-8	473	452
H = 2**				-7	-5	293	295	-5	8	478	478	-2	-7	298	310
-11	0	221	216	-7	-4	343	328	-5	9	432	419	-2	-6	460	451
-11	1	275	271	-7	-3	260	271	-5	10	360	368	-2	-5	395	389
-11	2	331	310	-7	-2	300	286	-5	11	254	236	-2	-4	416	397
-11	3	285	299	-7	-1	257	268	-5	12	179	182	-2	-3	476	465
-11	4	255	256	-7	0	259	273	-4	-10	235	242	-2	-2	751	713
-11	5	198	198	-7	1	403	401	-4	-9	283	285	-2	-1	278	276
-11	6	254	258	-7	2	560	554	-4	-8	387	381	-2	0	944	958
-10	-3	176	169	-7	3	631	619	-4	-7	323	342	-2	1	685	692
-10	-2	165	160	-7	4	497	494	-4	-6	424	410	-2	2	705	740
-10	-1	197	198	-7	5	483	497	-4	-5	326	327	-2	3	628	629
-10	0	280	267	-7	6	489	526	-4	-4	350	326	-2	4	687	703
-10	1	320	302	-7	7	418	399	-4	-3	379	387	-2	5	698	690
-10	2	261	253	-7	8	353	352	-4	-2	830	793	-2	6	463	460
-10	3	385	367	-7	9	396	403	-4	-1	555	566	-2	7	456	450
-10	4	343	332	-7	10	311	313	-4	0	201	173	-2	8	523	526
-10	5	275	262	-7	11	176	178	-4	1	171	161	-2	9	444	427
-10	6	297	284	-6	-9	165	183	-4	2	625	647	-2	10	362	349
-10	7	328	324	-6	-8	297	300	-4	3	632	631	-2	11	281	289
-10	8	291	278	-6	-7	358	368	-4	4	787	814	-2	12	113	111
-9	-5	214	228	-6	-6	297	282	-4	5	814	824	-1	-12	258	273
-9	-4	270	266	-6	-5	349	351	-4	6	470	499	-1	-11	353	338
-9	-3	244	246	-6	-4	319	338	-4	7	366	369	-1	-10	141	151
-9	-2	288	289	-6	-3	366	358	-4	8	357	354	-1	-9	317	300
-9	-1	343	355	-6	-2	292	273	-4	9	371	378	-1	-8	358	374
-9	0	262	241	-6	-1	310	320	-4	10	379	378	-1	-7	436	436
-9	1	217	212	-6	0	401	394	-4	11	246	237	-1	-6	456	433
-9	2	314	299	-6	1	486	480	-4	12	181	183	-1	-5	417	420
-9	3	318	312	-6	2	583	568	-3	-11	243	235	-1	-4	260	255
-9	4	320	325	-6	3	442	449	-3	-10	230	239	-1	-3	393	367
-9	5	262	247	-6	4	496	517	-3	-9	359	347	-1	-2	119	114
-9	6	343	323	-6	5	530	552	-3	-8	355	342	-1	-1	452	417
-9	7	289	299	-6	6	517	521	-3	-7	461	446	-1	0	531	569
-9	8	272	273	-6	7	430	428	-3	-6	317	319	-1	1	511	479
-9	9	260	255	-6	8	390	387	-3	-5	259	259	-1	2	1094	1149
-9	10	161	166	-6	9	417	421	-3	-4	184	194	-1	3	711	721
-8	-6	163	174	-6	10	277	276	-3	-3	517	482	-1	4	565	551
-8	-5	269	267	-6	11	153	156	-3	-2	407	415	-1	5	771	766
-8	-4	269	266	-6	12	138	146	-3	-1	780	752	-1	6	726	725
-8	-3	273	255	-5	-10	160	165	-3	0	504	493	-1	7	691	701
-8	-2	256	252	-5	-9	242	227	-3	1	270	287	-1	8	530	518
-8	-1	361	356	-5	-8	346	355	-3	2	645	658	-1	9	421	440
-8	0	271	252	-5	-7	449	445	-3	3	956	994	-1	10	369	365
-8	1	369	371	-5	-6	409	399	-3	4	866	890	-1	11	220	233
-8	2	511	510	-5	-5	211	219	-3	5	833	862	-1	12	237	236
-8	3	508	496	-5	-4	371	384	-3	6	567	578	0	-12	291	288
-8	4	511	502	-5	-3	440	422	-3	7	238	250	0	-11	298	281
-8	5	393	363	-5	-2	470	463	-3	8	382	394	0	-10	252	265
-8	6	500	492	-5	-1	501	497	-3	9	391	388	0	-9	380	369
-8	7	428	428	-5	0	156	195	-3	10	324	325	0	-8	529	541
-8	8	329	318	-5	1	383	399	-3	11	271	266	0	-7	541	542
-8	9	315	320	-5	2	464	467	-3	12	147	128	0	-6	495	503

Table 30. Continued

K	L	FOBS	FCAL
H = 2**			
0	-5	199	168
0	-4	148	142
0	-3	177	167
0	-2	682	656
0	-1	483	473
0	0	629	611
0	1	573	567
0	2	352	347
0	3	526	512
0	4	637	642
0	5	601	618
0	6	591	592
0	7	640	634
0	8	511	515
0	9	325	312
0	10	241	240
0	11	306	295
0	12	216	221
1	-13	184	167
1	-12	207	216
1	-11	340	332
1	-10	380	385
1	-9	393	404
1	-8	436	421
1	-7	533	528
1	-6	577	558
1	-5	295	314
1	-4	171	169
1	-3	749	748
1	-2	870	867
1	-1	608	609
1	0	189	193
1	1	1100	1103
1	2	531	527
1	3	909	910
1	4	887	863
1	5	602	602
1	6	592	587
1	7	470	467
1	8	391	368
1	9	239	232
1	10	305	285
1	11	244	243
1	12	195	185
2	-13	152	144
2	-12	189	177
2	-11	345	344
2	-10	521	514
2	-9	395	394
2	-8	279	282
2	-7	224	226
2	-6	656	634
2	-5	493	501
2	-4	449	465
2	-3	781	797
2	-2	818	848
2	-1	291	284
2	0	300	305
2	1	557	543
2	2	440	431
2	3	802	785
2	4	661	646
2	5	555	543
2	6	559	550
2	7	414	413
2	8	318	302
2	9	371	371
2	10	324	335
2	11	252	245
3	-13	174	164
3	-12	293	295
3	-11	228	230
3	-10	344	328
3	-9	338	346
3	-8	214	206
3	-7	297	296
3	-6	711	722
3	-5	990	1001
3	-4	385	397
3	-3	502	506
3	-2	383	380
3	-1	123	118
3	0	731	756
3	1	815	794
3	2	562	529
3	3	433	425
3	4	577	576
3	5	488	486
3	6	484	476
3	7	450	440
3	8	375	362
3	9	338	330
3	10	262	254
3	11	191	190
4	-13	233	254
4	-12	326	330
4	-11	332	346
4	-10	291	286
4	-9	351	356
4	-8	371	374
4	-7	369	388
4	-6	453	464
4	-5	464	463
4	-4	259	260
4	-3	97	121
4	-2	199	202
4	-1	384	385
4	0	539	548
4	1	808	794
4	2	368	368
4	3	156	160
4	4	396	392
4	5	465	464
4	6	501	499
4	7	392	378
4	8	327	330
4	9	244	251
4	10	188	188
5	-12	274	268
5	-11	336	332
5	-10	370	384
5	-9	383	379
5	-8	342	340
5	-7	429	423
5	-6	487	495
5	-5	355	356
5	-4	350	367
5	-3	424	407
5	-2	543	530
5	-1	266	257
5	0	431	438
5	1	380	379
5	2	327	335
5	3	283	286
5	4	353	348
5	5	483	478
5	6	469	471
5	7	348	352
5	8	157	158
5	9	153	154
6	-12	176	171
6	-11	261	273
6	-10	357	350
6	-9	347	353
6	-8	220	210
6	-7	490	486
6	-6	442	456
6	-5	405	440
6	-4	340	332
6	-3	321	314
6	-2	300	314
6	-1	370	358
6	0	418	412
6	1	316	305
6	2	386	411
6	3	396	387
6	4	270	282
6	5	405	413
6	6	333	327
6	7	243	254
6	8	212	211
7	-11	318	316
7	-10	356	356
7	-9	301	287
7	-8	278	294
7	-7	282	285
7	-6	384	396
7	-5	286	282
7	-4	469	451
7	-3	373	377
7	-2	182	176
7	-1	216	213
7	0	210	223
7	1	304	299
7	2	400	405
7	3	234	263
7	4	302	293
7	5	287	288
7	6	205	218
7	7	250	242
8	-11	283	278
8	-10	329	316
8	-9	352	352
8	-8	232	227
8	-7	325	335
8	-6	334	319
8	-5	247	231
8	-4	350	355
8	-3	376	367
8	-2	186	174
8	0	288	286
8	1	306	298
8	2	284	276
8	3	303	291
8	4	244	238
8	5	206	211
8	6	236	233
9	-10	277	277
9	-9	277	269
9	-8	284	276
9	-7	263	274
9	-6	249	237
9	-5	274	276
9	-4	193	215
9	-3	205	204
9	-2	190	198
9	-1	236	225
9	0	299	295
9	1	305	292
9	2	260	262
9	3	175	175
9	4	140	145
10	-8	279	275
10	-7	237	238
10	-6	199	208
10	-5	262	250
10	-4	241	238
10	-3	236	241
10	-2	234	249
10	-1	162	168
10	0	151	151
10	1	123	127
10	2	160	161
11	-4	209	218
11	-3	243	242
H = 3**			
-11	0	172	174

Table 30. Continued

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
H = 3**				-7	-1	190	187	-5	12	242	241	-2	-3	780	746
-11	1	270	254	-7	0	209	210	-4	-10	208	205	-2	-2	373	383
-11	2	186	189	-7	1	361	367	-4	-9	266	268	-2	-1	508	460
-11	3	203	192	-7	2	516	521	-4	-8	359	363	-2	0	288	296
-11	4	183	177	-7	3	397	396	-4	-7	356	366	-2	1	711	747
-11	5	194	190	-7	4	271	272	-4	-6	388	390	-2	2	307	287
-10	-3	162	167	-7	5	272	260	-4	-5	205	208	-2	3	543	540
-10	-2	143	145	-7	6	268	267	-4	-4	243	242	-2	4	517	512
-10	-1	156	167	-7	7	337	351	-4	-3	779	724	-2	5	384	401
-10	0	274	267	-7	8	344	339	-4	-2	496	512	-2	6	413	407
-10	1	222	225	-7	9	393	392	-4	-1	403	397	-2	7	447	453
-10	2	207	216	-7	10	289	282	-4	0	214	227	-2	8	499	485
-10	3	220	242	-7	11	170	177	-4	1	213	214	-2	9	408	396
-10	4	243	254	-6	-9	241	246	-4	2	380	371	-2	10	377	381
-10	5	226	210	-6	-8	287	298	-4	3	755	783	-2	11	362	351
-10	6	307	316	-6	-7	381	364	-4	4	654	675	-2	12	141	140
-10	7	303	299	-6	-6	323	331	-4	5	579	586	-1	-12	241	258
-10	8	307	286	-6	-5	328	317	-4	6	365	364	-1	-11	317	300
-9	-5	218	206	-6	-4	343	346	-4	7	384	392	-1	-10	199	219
-9	-4	224	225	-6	-3	300	297	-4	8	351	346	-1	-9	282	274
-9	-3	291	285	-6	-2	208	226	-4	9	421	411	-1	-8	455	443
-9	-2	303	291	-6	-1	239	234	-4	10	315	328	-1	-7	490	490
-9	-1	293	295	-6	0	328	319	-4	11	263	266	-1	-6	531	520
-9	0	197	206	-6	1	475	473	-4	12	246	249	-1	-5	568	567
-9	1	249	251	-6	2	386	381	-3	-11	258	257	-1	-4	414	419
-9	2	267	270	-6	3	324	328	-3	-10	258	265	-1	-3	201	205
-9	3	331	312	-6	4	346	352	-3	-9	361	365	-1	-2	696	672
-9	4	330	324	-6	5	377	387	-3	-8	417	403	-1	-1	1108	1113
-9	5	327	335	-6	6	376	388	-3	-7	434	436	-1	0	897	911
-9	6	377	375	-6	7	398	385	-3	-6	332	346	-1	1	717	720
-9	7	320	338	-6	8	384	395	-3	-5	284	285	-1	2	1052	1078
-9	8	315	326	-6	9	392	404	-3	-4	516	471	-1	3	692	704
-9	9	338	337	-6	10	195	213	-3	-3	487	503	-1	4	292	288
-8	-6	131	130	-6	11	170	181	-3	-2	577	546	-1	5	407	408
-8	-5	166	170	-6	12	212	213	-3	-1	238	235	-1	6	518	496
-8	-4	221	213	-5	-10	188	185	-3	0	346	353	-1	7	411	413
-8	-3	356	357	-5	-9	229	238	-3	1	334	330	-1	8	443	440
-8	-2	302	301	-5	-8	386	378	-3	2	604	614	-1	9	381	385
-8	-1	190	203	-5	-7	448	442	-3	3	529	533	-1	10	371	366
-8	0	170	171	-5	-6	456	446	-3	4	468	484	-1	11	344	329
-8	1	336	314	-5	-5	260	267	-3	5	311	315	-1	12	219	226
-8	2	485	486	-5	-4	291	264	-3	6	373	378	0	-12	254	260
-8	3	427	406	-5	-3	346	362	-3	7	248	246	0	-11	277	272
-8	4	379	374	-5	-2	493	487	-3	8	454	452	0	-10	236	222
-8	5	224	224	-5	-1	399	402	-3	9	383	390	0	-9	305	308
-8	6	322	327	-5	0	386	391	-3	10	348	347	0	-8	528	515
-8	7	361	372	-5	1	401	395	-3	11	335	337	0	-7	518	532
-8	8	378	395	-5	2	318	311	-3	12	197	201	0	-6	394	390
-8	9	397	375	-5	3	199	197	-2	-12	265	264	0	-5	459	467
-8	10	287	291	-5	4	443	454	-2	-11	324	331	0	-4	620	601
-7	-8	228	230	-5	5	479	467	-2	-10	242	238	0	-3	413	395
-7	-7	199	195	-5	6	358	365	-2	-9	258	274	0	-2	846	850
-7	-6	179	183	-5	7	423	429	-2	-8	477	469	0	-1	1660	1799
-7	-5	273	281	-5	8	488	489	-2	-7	374	378	0	0	793	772
-7	-4	390	375	-5	9	337	327	-2	-6	557	560	0	1	148	157
-7	-3	343	353	-5	10	258	260	-2	-5	613	610	0	2	240	229
-7	-2	318	335	-5	11	210	218	-2	-4	395	408	0	3	526	518

Table 30. Continued

K	L	FOBS	FCAL
**H =	3****		
0	4	371	366
0	5	676	673
0	6	523	518
0	7	445	446
0	8	414	406
0	9	216	226
0	10	285	263
0	11	358	338
0	12	182	193
1	-12	251	260
1	-11	320	318
1	-10	313	318
1	-9	341	347
1	-8	595	600
1	-7	589	581
1	-6	716	702
1	-5	523	505
1	-4	552	546
1	-3	682	683
1	-2	657	670
1	-1	1017	1083
1	0	146	144
1	1	154	157
1	2	650	634
1	3	625	597
1	4	820	794
1	5	404	420
1	6	457	445
1	7	272	260
1	8	274	258
1	9	284	286
1	10	316	304
1	11	301	287
2	-13	167	177
2	-12	263	248
2	-11	289	290
2	-10	433	414
2	-9	401	400
2	-8	396	369
2	-7	630	645
2	-6	760	770
2	-5	563	582
2	-4	495	484
2	-3	394	379
2	-2	470	485
2	-1	456	444
2	0	496	501
2	1	453	430
2	2	493	481
2	3	758	730
2	4	379	361
2	5	343	336
2	6	388	384
2	7	350	343
2	8	285	278
2	9	363	370
2	10	369	356
2	11	217	211
3	-13	179	183
3	-12	283	259
3	-11	205	205
3	-10	383	381
3	-9	460	462
3	-8	343	361
3	-7	511	519
3	-6	732	746
3	-5	849	850
3	-4	390	428
3	-3	267	247
3	-2	253	259
3	-1	415	422
3	0	421	426
3	1	278	296
3	2	351	344
3	3	301	298
3	4	416	394
3	5	337	327
3	6	433	423
3	7	378	378
3	8	276	274
3	9	323	317
3	10	261	263
4	-12	283	291
4	-11	355	360
4	-10	343	360
4	-9	463	473
4	-8	438	443
4	-7	518	506
4	-6	680	691
4	-5	737	745
4	-4	499	498
4	-3	180	168
4	-2	328	335
4	-1	483	471
4	0	548	561
4	1	445	439
4	2	393	389
4	3	233	214
4	4	259	269
4	5	270	255
4	6	266	268
4	7	261	267
4	8	250	234
4	9	216	221
5	-12	234	240
5	-11	302	292
5	-10	356	346
5	-9	403	414
5	-8	321	332
5	-7	504	509
5	-6	538	557
5	-5	397	395
5	-4	383	408
5	-3	462	456
5	-2	528	541
5	-1	514	510
5	0	425	427
5	1	334	324
5	2	258	257
5	3	304	319
5	4	307	316
5	5	361	372
5	6	353	353
5	7	351	342
5	8	176	185
5	9	152	148
6	-12	153	150
6	-11	277	267
6	-10	365	381
6	-9	392	395
6	-8	288	302
6	-7	393	399
6	-6	384	386
6	-5	380	390
6	-4	491	501
6	-3	367	370
6	-2	399	414
6	-1	316	315
6	0	252	264
6	1	187	186
6	2	279	278
6	3	274	284
6	4	293	301
6	5	334	342
6	6	307	294
6	7	221	230
6	8	218	227
7	-11	319	323
7	-10	329	331
7	-9	279	268
7	-8	278	279
7	-7	271	277
7	-6	427	420
7	-5	494	515
7	-4	581	568
7	-3	414	398
7	-2	193	207
7	-1	231	220
7	0	220	242
7	1	338	335
7	2	236	242
7	3	243	240
7	4	188	204
7	5	243	240
7	6	229	221
7	7	213	214
8	-10	275	276
8	-9	273	268
8	-8	260	253
8	-7	320	323
8	-6	428	427
8	-5	409	401
8	-4	361	359
8	-3	324	305
8	-2	131	122
8	-1	173	175
8	0	395	396
8	1	304	318
8	2	299	279
8	3	235	238
8	4	227	222
8	5	226	235
9	-9	267	274
9	-8	296	282
9	-7	280	286
9	-6	295	298
9	-5	335	314
9	-4	243	256
9	-3	166	171
9	-2	192	185
9	-1	303	298
9	0	320	331
9	1	311	307
9	2	234	243
9	3	181	186
10	-7	256	254
10	-6	277	270
10	-5	326	324
10	-4	328	321
10	-3	269	254
10	-2	230	220
10	-1	189	200
10	0	186	182
10	1	148	165
**H =	4****		
-11	1	278	282
-11	2	155	172
-11	3	143	132
-11	4	130	129
-11	5	180	173
-10	-3	228	226
-10	-2	228	231
-10	-1	225	226
-10	0	279	277
-10	1	239	245
-10	2	193	193
-10	3	170	158
-10	4	156	163
-10	5	193	189
-10	6	296	290
-10	7	254	260
-10	8	208	202
-9	-5	236	233
-9	-4	307	296
-9	-3	321	341
-9	-2	330	350
-9	-1	247	239

Table 30. Continued

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
H = 4**				-6	1	371	350	-3	-11	187	196	-1	-3	395	364
-9	0	156	153	-6	2	410	400	-3	-10	249	252	-1	-2	678	667
-9	1	226	215	-6	3	241	225	-3	-9	252	273	-1	-1	919	885
-9	2	193	186	-6	4	205	198	-3	-8	438	425	-1	0	896	930
-9	3	237	228	-6	5	232	233	-3	-7	535	526	-1	1	608	612
-9	4	219	220	-6	6	208	222	-3	-6	465	458	-1	2	329	351
-9	5	227	234	-6	7	287	298	-3	-5	485	470	-1	3	517	537
-9	6	318	304	-6	8	395	378	-3	-4	661	663	-1	4	589	569
-9	7	330	303	-6	9	303	302	-3	-3	1044	1016	-1	5	384	374
-9	8	214	204	-6	10	184	186	-3	-2	488	498	-1	6	324	322
-9	9	189	190	-6	11	198	196	-3	-1	448	439	-1	7	229	242
-8	-6	203	204	-5	-10	190	198	-3	0	456	469	-1	8	342	317
-8	-5	284	283	-5	-9	223	219	-3	1	198	199	-1	9	347	338
-8	-4	292	304	-5	-8	283	279	-3	2	538	556	-1	10	285	283
-8	-3	425	427	-5	-7	338	333	-3	3	475	477	-1	11	241	242
-8	-2	368	376	-5	-6	341	334	-3	4	546	556	-1	12	189	187
-8	-1	178	181	-5	-5	307	283	-3	5	269	261	0	-12	220	231
-8	0	161	165	-5	-4	342	367	-3	6	245	223	0	-11	243	243
-8	1	310	302	-5	-3	553	562	-3	7	304	308	0	-10	275	265
-8	2	404	407	-5	-2	500	503	-3	8	249	231	0	-9	241	255
-8	3	303	302	-5	-1	609	597	-3	9	297	297	0	-8	518	489
-8	4	224	228	-5	0	564	546	-3	10	301	299	0	-7	540	540
-8	6	93	78	-5	1	533	523	-3	11	295	288	0	-6	527	541
-8	7	279	249	-5	2	367	365	-3	12	197	198	0	-5	772	762
-8	8	281	273	-5	3	173	178	-2	-11	266	271	0	-4	699	692
-8	9	226	236	-5	4	310	318	-2	-10	213	195	0	-3	746	748
-8	10	225	230	-5	5	333	348	-2	-9	263	261	0	-2	1132	1124
-7	-8	216	220	-5	6	199	213	-2	-8	463	448	0	-1	1338	1399
-7	-7	255	259	-5	7	383	381	-2	-7	557	545	0	0	866	830
-7	-6	272	274	-5	8	426	440	-2	-6	618	613	0	1	603	573
-7	-5	316	309	-5	9	368	375	-2	-5	648	633	0	2	65	68
-7	-4	455	458	-5	10	267	274	-2	-4	676	655	0	3	309	315
-7	-3	483	457	-5	11	225	233	-2	-3	502	515	0	4	362	371
-7	-2	396	400	-5	12	253	243	-2	-2	524	511	0	5	331	327
-7	-1	199	203	-4	-10	200	195	-2	-1	501	500	0	6	261	256
-7	0	266	265	-4	-9	223	240	-2	0	330	313	0	7	220	220
-7	1	377	365	-4	-8	268	260	-2	1	700	719	0	8	329	318
-7	2	431	436	-4	-7	382	373	-2	2	381	391	0	9	371	341
-7	3	309	303	-4	-6	424	421	-2	3	453	467	0	10	267	289
-7	4	72	80	-4	-5	271	283	-2	4	523	507	0	11	278	276
-7	5	51	56	-4	-4	620	604	-2	5	451	452	1	-12	203	211
-7	6	146	104	-4	-3	745	747	-2	6	358	364	1	-11	272	265
-7	7	321	327	-4	-2	680	640	-2	7	454	446	1	-10	246	232
-7	8	401	412	-4	-1	499	483	-2	8	406	422	1	-9	323	318
-7	9	322	317	-4	0	390	375	-2	9	358	340	1	-8	642	642
-7	10	216	225	-4	1	110	121	-2	10	294	296	1	-7	554	563
-7	11	185	186	-4	2	139	148	-2	11	247	237	1	-6	576	570
-6	-9	230	230	-4	3	525	528	-2	12	148	153	1	-5	691	690
-6	-8	285	291	-4	4	331	336	-1	-12	210	212	1	-4	566	569
-6	-7	359	379	-4	5	331	326	-1	-11	249	248	1	-3	664	666
-6	-6	360	378	-4	6	316	323	-1	-10	270	261	1	-2	783	806
-6	-5	283	294	-4	7	313	320	-1	-9	238	240	1	-1	924	932
-6	-4	516	515	-4	8	328	352	-1	-8	397	391	1	0	398	382
-6	-3	470	475	-4	9	359	361	-1	-7	648	651	1	1	290	288
-6	-2	290	283	-4	10	321	307	-1	-6	605	603	1	2	300	291
-6	-1	377	392	-4	11	232	235	-1	-5	576	557	1	3	351	356
-6	0	330	343	-4	12	267	263	-1	-4	461	449	1	4	516	498

Table 30. Continued

K	L	FOBS	FCAL
**H =	4****		
1	5	372	350
1	6	414	399
1	7	243	243
1	8	298	279
1	9	351	351
1	10	298	293
1	11	218	219
2	-12	266	257
2	-11	296	305
2	-10	302	306
2	-9	293	308
2	-8	382	372
2	-7	472	478
2	-6	476	467
2	-5	473	458
2	-4	423	447
2	-3	732	754
2	-2	763	795
2	-1	386	397
2	0	395	406
2	1	416	431
2	2	494	470
2	3	366	370
2	4	481	460
2	5	429	404
2	6	265	257
2	7	301	298
2	8	279	265
2	9	347	339
2	10	286	283
3	-12	239	244
3	-11	200	187
3	-10	178	187
3	-9	227	203
3	-8	282	281
3	-7	520	512
3	-6	611	652
3	-5	681	682
3	-4	598	596
3	-3	458	476
3	-2	658	670
3	-1	668	678
3	0	441	458
3	1	625	601
3	2	397	410
3	3	192	181
3	4	333	333
3	5	362	364
3	6	377	375
3	7	268	264
3	8	193	199
3	9	233	224
3	10	179	177
4	-12	243	238
4	-11	237	233
4	-10	186	193
4	-9	250	256
4	-8	349	363
4	-7	499	504
4	-6	614	614
4	-5	572	586
4	-4	458	467
4	-3	278	290
4	-2	669	653
4	-1	707	698
4	0	652	671
4	1	505	512
4	2	443	427
4	3	259	254
4	4	304	286
4	5	371	366
4	6	267	269
4	7	195	197
4	8	164	160
4	9	170	177
5	-12	198	204
5	-11	262	267
5	-10	274	283
5	-9	314	318
5	-8	233	243
5	-7	357	342
5	-6	483	501
5	-5	408	417
5	-4	398	419
5	-3	455	464
5	-2	516	507
5	-1	546	549
5	0	429	446
5	1	338	362
5	2	239	243
5	3	338	345
5	4	345	353
5	5	372	375
5	6	209	233
5	7	231	241
5	8	206	210
6	-12	167	161
6	-11	236	237
6	-10	259	261
6	-9	267	264
6	-8	279	287
6	-7	277	279
6	-6	398	388
6	-5	478	467
6	-4	593	606
6	-3	457	458
6	-2	440	441
6	-1	452	459
6	0	401	397
6	1	391	406
6	2	376	374
6	3	305	313
6	4	334	319
6	5	226	235
6	6	188	190
6	7	210	205
7	-11	232	225
7	-10	168	174
7	-9	199	202
7	-8	251	236
7	-7	198	202
7	-6	392	370
7	-5	554	556
7	-4	659	656
7	-3	526	519
7	-2	322	325
7	-1	405	400
7	0	473	464
7	1	537	541
7	2	260	253
7	3	197	197
7	4	127	140
7	5	141	145
7	6	222	228
8	-10	204	202
8	-9	165	169
8	-8	204	198
8	-7	251	249
8	-6	348	350
8	-5	449	437
8	-4	417	427
8	-3	370	353
8	-2	266	270
8	-1	308	315
8	0	453	449
8	1	308	328
8	2	206	209
8	3	113	124
8	4	153	147
9	-9	232	227
9	-8	227	226
9	-7	264	247
9	-6	328	325
9	-5	366	351
9	-4	282	268
9	-3	243	255
9	-2	319	315
9	-1	327	343
9	0	316	335
9	1	251	255
9	2	168	169
9	3	179	177
10	-6	295	287
10	-5	295	294
10	-4	317	303
10	-3	297	284
10	-2	282	279
10	-1	293	277
10	0	258	249
**H =	5****		
-11	2	191	195
-11	3	148	151
-10	-2	288	285
-10	-1	298	284
-10	0	303	289
-10	1	290	280
-10	2	254	253
-10	3	184	177
-10	4	131	131
-10	5	162	150
-10	6	214	209
-10	7	143	164
-9	-5	263	266
-9	-4	331	328
-9	-3	364	365
-9	-2	345	354
-9	-1	265	252
-9	0	207	205
-9	1	197	210
-9	2	279	280
-9	3	232	226
-9	4	176	170
-9	5	185	172
-9	6	261	254
-9	7	286	299
-9	8	108	113
-9	9	143	152
-8	-6	220	223
-8	-5	301	292
-8	-4	311	310
-8	-3	314	307
-8	-2	363	376
-8	-1	283	259
-8	0	227	218
-8	1	406	402
-8	2	361	356
-8	3	302	287
-8	4	198	192
-8	5	209	205
-8	6	232	240
-8	7	291	291
-8	8	178	187
-8	9	128	141
-8	10	181	165
-7	-7	215	218
-7	-6	275	271
-7	-5	321	323
-7	-4	396	392
-7	-3	367	371
-7	-2	484	491
-7	-1	326	325
-7	0	415	397
-7	1	479	470
-7	2	485	465
-7	3	359	373
-7	4	211	220
-7	5	216	222

Table 30. Continued

K	L	FOBS	FCAL
H = 5**			
-7	6	201	178
-7	7	257	243
-7	8	258	256
-7	9	200	206
-7	10	164	171
-6	-8	256	261
-6	-7	352	338
-6	-6	341	345
-6	-5	351	334
-6	-4	360	378
-6	-3	513	487
-6	-2	431	436
-6	-1	449	442
-6	0	426	425
-6	1	536	543
-6	2	458	478
-6	3	389	421
-6	4	356	375
-6	5	344	338
-6	6	241	239
-6	7	301	288
-6	8	290	299
-6	9	247	247
-6	10	162	171
-6	11	146	150
-5	-9	235	233
-5	-8	326	329
-5	-7	273	282
-5	-6	392	378
-5	-5	237	255
-5	-4	362	328
-5	-3	539	547
-5	-2	661	649
-5	-1	481	477
-5	0	411	441
-5	1	456	462
-5	2	457	461
-5	3	306	303
-5	4	368	379
-5	5	286	284
-5	6	256	275
-5	7	279	291
-5	8	355	355
-5	9	323	323
-5	10	230	227
-5	11	169	187
-4	-10	238	241
-4	-9	275	269
-4	-8	180	188
-4	-7	333	332
-4	-6	386	384
-4	-5	500	474
-4	-4	505	514
-4	-3	896	861
-4	-2	749	763
-4	-1	498	495
-4	0	391	400
-4	1	436	452
-4	2	580	579
-4	3	657	671
-4	4	350	363
-4	5	308	321
-4	6	215	207
-4	7	166	168
-4	8	254	257
-4	9	395	387
-4	10	265	246
-4	11	128	128
-3	-11	189	190
-3	-10	284	267
-3	-9	268	273
-3	-8	315	319
-3	-7	385	365
-3	-6	420	408
-3	-5	414	429
-3	-4	579	565
-3	-3	783	771
-3	-2	795	768
-3	-1	587	578
-3	0	530	535
-3	1	456	465
-3	2	878	890
-3	3	683	678
-3	4	549	554
-3	5	191	198
-3	6	232	230
-3	7	232	233
-3	8	248	263
-3	9	325	318
-3	10	213	223
-3	11	156	162
-2	-11	214	215
-2	-10	203	199
-2	-9	294	301
-2	-8	342	338
-2	-7	425	422
-2	-6	399	380
-2	-5	565	552
-2	-4	496	493
-2	-3	697	673
-2	-2	546	556
-2	-1	694	689
-2	0	576	590
-2	1	416	453
-2	2	616	626
-2	3	748	750
-2	4	359	356
-2	5	226	238
-2	6	314	319
-2	7	423	436
-2	8	347	333
-2	9	220	224
-2	10	185	186
-2	11	107	96
-1	-12	197	205
-1	-11	160	172
-1	-10	209	204
-1	-9	270	258
-1	-8	359	366
-1	-7	498	484
-1	-6	483	485
-1	-5	527	500
-1	-4	622	595
-1	-3	446	464
-1	-2	660	655
-1	-1	1036	1026
-1	0	891	911
-1	1	310	312
-1	2	442	458
-1	3	573	573
-1	4	649	648
-1	5	410	413
-1	6	352	343
-1	7	241	240
-1	8	178	198
-1	9	238	205
-1	10	157	149
-1	11	175	173
0	-12	181	173
0	-11	106	118
0	-10	204	189
0	-9	276	274
0	-8	371	372
0	-7	388	397
0	-6	324	325
0	-5	423	430
0	-4	430	430
0	-3	734	732
0	-2	1051	1069
0	-1	1158	1205
0	0	908	883
0	1	556	538
0	2	251	243
0	3	448	445
0	4	700	705
0	5	410	409
0	6	308	300
0	7	163	143
0	8	171	175
0	9	332	330
0	10	277	285
0	11	211	224
1	-12	184	185
1	-11	216	230
1	-10	262	250
1	-9	193	193
1	-8	376	360
1	-7	342	347
1	-6	271	290
1	-5	562	551
1	-4	497	528
1	-3	578	587
1	-2	649	643
1	-1	613	656
1	0	495	453
1	1	408	417
1	2	554	555
1	3	640	598
1	4	466	450
1	5	372	378
1	6	415	412
1	7	269	268
1	8	246	242
1	9	378	376
1	10	265	284
2	-12	223	227
2	-11	213	211
2	-10	236	228
2	-9	186	189
2	-8	244	252
2	-7	374	370
2	-6	435	431
2	-5	651	654
2	-4	601	630
2	-3	751	775
2	-2	598	609
2	-1	457	479
2	0	654	646
2	1	644	621
2	2	709	714
2	3	459	465
2	4	380	381
2	5	345	344
2	6	367	355
2	7	271	282
2	8	233	233
2	9	327	324
2	10	218	224
3	-12	169	169
3	-11	101	107
3	-10	191	203
3	-9	259	268
3	-8	195	192
3	-7	413	408
3	-6	570	572
3	-5	609	633
3	-4	529	556
3	-3	512	541
3	-2	572	580
3	-1	809	814
3	0	769	761
3	1	764	735
3	2	464	443
3	3	261	274
3	4	313	316
3	5	434	422
3	6	385	373

K	L	FOBS	FCAL
H = 5**			
3	7	245	240
3	8	241	239
3	9	230	228
4	-12	250	267
4	-11	172	176
4	-10	120	116
4	-9	175	156
4	-8	315	324
4	-7	350	348
4	-6	575	584
4	-5	431	439
4	-4	489	481
4	-3	476	476
4	-2	643	646
4	-1	766	793
4	0	774	781
4	1	476	497
4	2	233	248
4	3	232	234
4	4	360	360
4	5	371	386
4	6	318	302
4	7	214	202
4	8	154	156
4	9	185	185
5	-12	210	213
5	-11	178	189
5	-10	155	158
5	-9	230	226
5	-8	232	238
5	-7	357	366
5	-6	396	372
5	-5	338	343
5	-4	364	358
5	-3	561	554
5	-2	528	530
5	-1	541	548
5	0	540	538
5	1	372	382
5	2	252	247
5	3	413	409
5	4	422	433
5	5	431	433
5	6	250	247
5	7	134	134
5	8	172	179
6	-11	213	215
6	-10	173	169
6	-9	147	145
6	-8	307	300
6	-7	211	211
6	-6	309	320
6	-5	371	361
6	-4	394	390
6	-3	476	471
6	-2	472	456
6	-1	486	481
6	0	437	428
6	1	439	457
6	2	364	358
6	3	253	246
6	4	386	387
6	5	325	333
6	6	169	174
6	7	135	138
7	-10	135	136
7	-9	134	141
7	-8	166	165
7	-7	198	193
7	-6	296	306
7	-5	376	360
7	-4	494	471
7	-3	495	490
7	-2	268	256
7	-1	327	330
7	0	403	390
7	1	406	418
7	2	279	293
7	3	236	226
7	4	236	230
7	5	188	197
8	-9	121	119
8	-8	146	146
8	-7	245	224
8	-6	260	257
8	-5	338	325
8	-4	371	377
8	-3	278	275
8	-2	210	210
8	-1	267	272
8	0	370	362
8	1	350	359
8	2	281	290
8	3	152	143
8	4	107	118
9	-8	121	130
9	-7	199	189
9	-6	231	224
9	-5	238	229
9	-4	211	202
9	-3	216	229
9	-2	316	300
9	-1	350	341
9	0	369	355
9	1	282	292
9	2	195	202
10	-4	230	222
10	-3	241	251
10	-2	266	270
H = 6**			
-10	-2	250	254
-10	-1	331	322
-10	0	332	325
-10	1	310	305
-10	2	321	315
-10	3	260	266
-10	4	182	184
-10	5	256	253
-10	6	251	255
-9	-4	266	268
-9	-3	298	286
-9	-2	298	288
-9	-1	315	317
-9	0	271	260
-9	1	245	236
-9	2	310	308
-9	3	308	302
-9	4	298	296
-9	5	285	296
-9	6	245	267
-9	7	259	262
-9	8	157	154
-8	-6	162	162
-8	-5	251	250
-8	-4	367	358
-8	-3	272	273
-8	-2	278	276
-8	-1	297	303
-8	0	382	370
-8	1	510	494
-8	2	470	466
-8	3	435	434
-8	4	326	319
-8	5	298	295
-8	6	209	213
-8	7	257	261
-8	8	255	242
-8	9	155	146
-7	-7	139	142
-7	-6	187	200
-7	-5	289	276
-7	-4	367	381
-7	-3	289	289
-7	-2	291	275
-7	-1	401	400
-7	0	569	568
-7	1	704	713
-7	2	588	590
-7	3	424	428
-7	4	308	304
-7	5	339	329
-7	6	241	251
-7	7	237	243
-7	8	239	240
-7	9	198	198
-7	10	101	105
-6	-8	236	243
-6	-7	253	265
-6	-6	252	242
-6	-5	259	250
-6	-4	295	281
-6	-3	363	375
-6	-2	419	398
-6	-1	460	466
-6	0	534	544
-6	1	609	608
-6	2	486	481
-6	3	398	385
-6	4	391	387
-6	5	345	350
-6	6	325	325
-6	7	248	256
-6	8	245	253
-6	9	148	148
-6	10	126	125
-5	-9	231	235
-5	-8	344	344
-5	-7	297	300
-5	-6	305	304
-5	-5	220	208
-5	-4	259	267
-5	-3	481	492
-5	-2	590	593
-5	-1	468	466
-5	0	469	471
-5	1	456	457
-5	2	411	434
-5	3	551	561
-5	4	529	523
-5	5	397	408
-5	6	336	331
-5	7	316	313
-5	8	279	276
-5	9	207	202
-5	10	154	154
-5	11	165	173
-4	-10	207	228
-4	-9	300	287
-4	-8	256	257
-4	-7	296	303
-4	-6	160	150
-4	-5	201	203
-4	-4	441	414
-4	-3	613	599
-4	-2	522	514
-4	-1	429	419
-4	0	505	484
-4	1	448	447
-4	2	763	796
-4	3	763	791
-4	4	519	523
-4	5	394	382
-4	6	229	250
-4	7	203	193
-4	8	290	290
-4	9	296	316
-4	10	159	167

Table 30. Continued

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
H = 6**				-1	-1	605	583	1	9	263	259	4	-1	596	579
-4	11	126	124	-1	0	573	617	1	10	253	258	4	0	602	594
-3	-10	244	246	-1	1	603	617	2	-12	208	202	4	1	531	524
-3	-9	327	320	-1	2	815	791	2	-11	179	178	4	2	353	344
-3	-8	236	232	-1	3	793	790	2	-10	338	326	4	3	374	383
-3	-7	138	148	-1	4	516	529	2	-9	262	256	4	4	417	403
-3	-6	208	225	-1	5	421	388	2	-8	219	218	4	5	388	379
-3	-5	398	373	-1	6	379	382	2	-7	423	416	4	6	329	331
-3	-4	462	470	-1	7	451	455	2	-6	361	386	4	7	232	234
-3	-3	627	603	-1	8	346	341	2	-5	338	326	4	8	136	136
-3	-2	618	605	-1	9	263	262	2	-4	346	336	5	-11	201	204
-3	-1	442	455	-1	10	222	215	2	-3	333	320	5	-10	212	211
-3	0	530	532	-1	11	195	189	2	-2	554	566	5	-9	180	173
-3	1	677	684	0	-12	189	183	2	-1	578	568	5	-8	203	189
-3	2	685	706	0	-11	120	112	2	0	535	516	5	-7	315	336
-3	3	593	608	0	-10	199	194	2	1	531	542	5	-6	228	228
-3	4	450	468	0	-9	310	302	2	2	664	627	5	-5	195	201
-3	5	306	315	0	-8	273	285	2	3	577	569	5	-4	202	220
-3	6	230	229	0	-7	199	187	2	4	472	472	5	-3	302	307
-3	7	239	255	0	-6	235	224	2	5	480	466	5	-2	334	341
-3	8	248	233	0	-5	287	281	2	6	342	322	5	-1	392	403
-3	9	251	251	0	-4	187	188	2	7	247	254	5	0	381	361
-3	10	190	197	0	-3	490	519	2	8	268	271	5	1	243	262
-3	11	172	167	0	-2	751	775	2	9	301	300	5	2	278	288
-2	-11	158	158	0	-1	651	681	3	-12	163	169	5	3	388	388
-2	-10	202	206	0	0	452	446	3	-11	179	180	5	4	429	438
-2	-9	318	303	0	1	616	607	3	-10	277	276	5	5	387	385
-2	-8	235	251	0	2	682	657	3	-9	287	290	5	6	261	253
-2	-7	300	285	0	3	483	486	3	-8	238	247	5	7	146	156
-2	-6	339	332	0	4	608	630	3	-7	382	377	6	-11	242	250
-2	-5	455	443	0	5	521	511	3	-6	430	418	6	-10	181	196
-2	-4	411	398	0	6	490	480	3	-5	394	415	6	-9	125	120
-2	-3	562	538	0	7	417	397	3	-4	279	249	6	-8	289	288
-2	-2	484	445	0	8	212	224	3	-3	229	224	6	-7	221	208
-2	-1	588	584	0	9	301	283	3	-2	443	434	6	-6	238	231
-2	0	637	674	0	10	246	240	3	-1	669	686	6	-5	266	261
-2	1	405	411	1	-12	193	191	3	0	456	473	6	-4	281	270
-2	2	691	696	1	-11	187	206	3	1	549	530	6	-3	324	333
-2	3	708	736	1	-10	272	274	3	2	576	569	6	-2	305	306
-2	4	378	367	1	-9	302	299	3	3	383	377	6	-1	317	310
-2	5	322	321	1	-8	354	354	3	4	460	453	6	0	287	298
-2	6	365	377	1	-7	398	393	3	5	529	507	6	1	398	399
-2	7	373	350	1	-6	304	281	3	6	335	339	6	2	305	317
-2	8	280	280	1	-5	307	310	3	7	240	228	6	3	335	341
-2	9	262	251	1	-4	335	336	3	8	232	226	6	4	389	409
-2	10	227	236	1	-3	351	364	3	9	206	201	6	5	283	280
-2	11	149	155	1	-2	699	710	4	-12	221	231	6	6	172	180
-1	-11	156	145	1	-1	664	680	4	-11	162	166	7	-10	144	136
-1	-10	186	194	1	0	373	386	4	-10	169	181	7	-9	73	88
-1	-9	321	312	1	1	578	544	4	-9	174	168	7	-8	162	159
-1	-8	283	278	1	2	704	708	4	-8	198	179	7	-7	236	238
-1	-7	258	257	1	3	561	553	4	-7	218	211	7	-6	260	258
-1	-6	286	274	1	4	537	532	4	-6	409	427	7	-5	269	259
-1	-5	340	337	1	5	465	453	4	-5	202	208	7	-4	210	199
-1	-4	473	466	1	6	288	278	4	-4	211	207	7	-3	251	253
-1	-3	460	448	1	7	209	188	4	-3	262	263	7	-2	147	140
-1	-2	690	686	1	8	188	188	4	-2	366	366	7	-1	247	254

Table 30. Continued

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
H = 6**				-8	6	282	282	-5	9	206	214	-2	3	568	561
7	0	399	387	-8	7	316	311	-5	10	171	166	-2	4	461	457
7	1	340	350	-8	8	307	313	-4	-9	220	231	-2	5	404	398
7	2	285	288	-7	-7	122	124	-4	-8	268	265	-2	6	563	555
7	3	268	275	-7	-6	200	191	-4	-7	261	261	-2	7	461	451
7	4	266	272	-7	-5	253	255	-4	-6	128	130	-2	8	346	333
8	-9	125	131	-7	-4	358	346	-4	-5	293	288	-2	9	248	256
8	-8	143	161	-7	-3	236	234	-4	-4	450	437	-2	10	243	239
8	-7	191	181	-7	-2	126	126	-4	-3	327	314	-1	-11	193	194
8	-6	155	155	-7	-1	311	309	-4	-2	296	298	-1	-10	215	222
8	-5	172	154	-7	0	465	438	-4	-1	301	302	-1	-9	302	296
8	-4	138	137	-7	1	526	500	-4	0	353	341	-1	-8	336	319
8	-3	153	152	-7	2	354	350	-4	1	439	448	-1	-7	337	326
8	-2	253	240	-7	3	243	239	-4	2	679	707	-1	-6	138	136
8	-1	296	297	-7	4	300	303	-4	3	582	576	-1	-5	162	171
8	0	376	376	-7	5	343	350	-4	4	491	500	-1	-4	208	197
8	1	318	309	-7	6	324	317	-4	5	433	450	-1	-3	334	324
8	2	256	265	-7	7	299	303	-4	6	376	370	-1	-2	603	583
8	3	218	210	-7	8	317	305	-4	7	279	296	-1	-1	368	363
9	-7	117	117	-7	9	212	216	-4	8	336	325	-1	0	542	530
9	-6	131	134	-6	-8	216	230	-4	9	239	239	-1	1	414	438
9	-5	132	128	-6	-7	183	183	-4	10	185	176	-1	2	318	321
9	-4	152	146	-6	-6	169	176	-3	-10	181	189	-1	3	643	650
9	-3	171	181	-6	-5	263	266	-3	-9	305	304	-1	4	607	609
9	-2	251	251	-6	-4	233	242	-3	-8	298	288	-1	5	441	439
9	-1	302	293	-6	-3	297	309	-3	-7	163	148	-1	6	465	463
9	0	258	260	-6	-2	280	282	-3	-6	134	123	-1	7	452	447
H = 7**				-6	-1	262	266	-3	-5	276	273	-1	8	282	281
-10	-1	266	276	-6	0	357	348	-3	-4	346	328	-1	9	251	250
-10	0	230	236	-6	1	524	510	-3	-3	324	321	-1	10	251	260
-10	1	240	240	-6	2	443	450	-3	-2	328	317	0	-11	205	208
-10	2	298	285	-6	3	203	203	-3	-1	233	208	0	-10	238	244
-10	3	282	276	-6	4	395	416	-3	0	398	415	0	-9	308	288
-10	4	258	260	-6	5	383	384	-3	1	593	606	0	-8	394	379
-10	5	320	312	-6	6	312	307	-3	2	607	614	0	-7	255	261
-9	-3	211	217	-6	7	340	332	-3	3	621	638	0	-6	231	223
-9	-2	229	227	-6	8	294	310	-3	4	475	479	0	-5	176	181
-9	-1	239	243	-6	9	156	167	-3	5	390	400	0	-4	297	298
-9	0	213	212	-6	10	162	166	-3	6	352	354	0	-3	728	694
-9	1	267	262	-5	-9	230	238	-3	7	387	372	0	-2	700	688
-9	2	361	361	-5	-8	233	235	-3	8	261	267	0	-1	343	342
-9	3	344	347	-5	-7	180	190	-3	9	303	305	0	0	225	230
-9	4	293	289	-5	-6	207	197	-3	10	253	255	0	1	291	296
-9	5	277	291	-5	-5	234	233	-2	-11	193	194	0	2	483	476
-9	6	311	291	-5	-4	310	304	-2	-10	201	205	0	3	537	512
-9	7	252	244	-5	-3	335	313	-2	-9	307	292	0	4	565	553
-8	-5	230	231	-5	-2	347	342	-2	-8	341	340	0	5	356	342
-8	-4	260	271	-5	-1	225	221	-2	-7	316	309	0	6	341	336
-8	-3	223	218	-5	0	304	308	-2	-6	251	246	0	7	320	315
-8	-2	197	197	-5	1	460	462	-2	-5	271	262	0	8	258	255
-8	-1	281	279	-5	2	404	392	-2	-4	258	261	0	9	226	229
-8	0	408	403	-5	3	401	412	-2	-3	113	115	0	10	228	207
-8	1	445	448	-5	4	359	371	-2	-2	238	240	1	-11	248	242
-8	2	368	377	-5	5	416	421	-2	-1	369	355	1	-10	280	261
-8	3	325	331	-5	6	371	388	-2	0	521	508	1	-9	347	348
-8	4	286	285	-5	7	434	433	-2	1	546	562	1	-8	299	289
-8	5	304	311	-5	8	336	356	-2	2	467	477	1	-7	308	309

Table 30. Continued

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
H = 7**				3	8	257	247	7	-6	267	267	-7	6	331	326
1	-6	250	250	4	-11	211	214	7	-5	293	306	-7	7	349	349
1	-5	206	206	4	-10	266	270	7	-4	197	205	-7	8	310	323
1	-4	261	259	4	-9	280	297	7	-3	124	122	-6	-7	205	210
1	-3	461	449	4	-8	312	322	7	-2	133	127	-6	-6	268	263
1	-2	550	546	4	-7	291	308	7	-1	216	214	-6	-5	219	216
1	-1	275	290	4	-6	178	185	7	0	323	333	-6	-4	129	128
1	0	346	323	4	-5	92	90	7	1	231	238	-6	-3	205	210
1	1	481	466	4	-4	75	101	7	2	204	204	-6	-2	150	150
1	2	660	643	4	-3	216	233	7	3	236	236	-6	-1	262	255
1	3	638	615	4	-2	301	295	8	-8	170	175	-6	0	417	403
1	4	452	423	4	-1	380	404	8	-7	222	215	-6	1	338	332
1	5	297	288	4	0	361	363	8	-6	240	231	-6	2	222	243
1	6	251	254	4	1	230	237	8	-5	240	249	-6	3	144	137
1	7	317	311	4	2	211	224	8	-4	123	119	-6	4	370	380
1	8	268	261	4	3	407	393	8	-3	67	65	-6	5	356	339
1	9	215	214	4	4	278	272	8	-2	190	186	-6	6	343	354
2	-11	240	243	4	5	294	299	8	-1	229	238	-6	7	348	363
2	-10	285	288	4	6	233	247	8	0	284	286	-6	8	301	298
2	-9	282	255	4	7	257	250	8	1	212	206	-6	9	199	202
2	-8	150	160	5	-11	273	277	9	-4	154	141	-5	-8	218	216
2	-7	329	330	5	-10	249	260	9	-3	135	136	-5	-7	228	226
2	-6	378	366	5	-9	231	229	9	-2	180	194	-5	-6	202	205
2	-5	213	190	5	-8	278	267	**H = 8****				-5	-5	204	213
2	-4	287	294	5	-7	286	284	-9	-2	159	166	-5	-4	358	353
2	-3	269	294	5	-6	197	191	-9	-1	117	126	-5	-3	401	388
2	-2	223	222	5	-5	270	258	-9	0	91	102	-5	-2	334	324
2	-1	341	356	5	-4	297	281	-9	1	196	195	-5	-1	312	301
2	0	417	418	5	-3	317	305	-9	2	286	262	-5	0	325	317
2	1	425	392	5	-2	286	277	-9	3	276	259	-5	1	290	277
2	2	459	442	5	-1	336	334	-9	4	246	256	-5	2	170	187
2	3	595	583	5	0	269	279	-9	5	295	296	-5	3	313	341
2	4	430	407	5	1	216	220	-9	6	302	314	-5	4	316	303
2	5	307	303	5	2	313	323	-8	-5	192	202	-5	5	394	411
2	6	257	251	5	3	282	297	-8	-4	204	213	-5	6	356	356
2	7	306	308	5	4	354	362	-8	-3	184	192	-5	7	332	336
2	8	284	286	5	5	228	246	-8	-2	103	106	-5	8	360	360
2	9	252	249	5	6	215	217	-8	-1	91	83	-5	9	257	252
3	-11	207	209	6	-10	192	197	-8	0	215	218	-4	-9	215	212
3	-10	170	164	6	-9	185	181	-8	1	278	279	-4	-8	212	215
3	-9	225	227	6	-8	230	235	-8	2	266	242	-4	-7	212	205
3	-8	329	331	6	-7	226	240	-8	3	234	232	-4	-6	200	201
3	-7	340	366	6	-6	229	215	-8	4	221	220	-4	-5	343	330
3	-6	346	347	6	-5	261	263	-8	5	220	218	-4	-4	524	507
3	-5	191	187	6	-4	235	244	-8	6	339	328	-4	-3	416	402
3	-4	60	38	6	-3	189	196	-8	7	300	310	-4	-2	170	172
3	-3	103	100	6	-2	208	192	-7	-6	213	224	-4	-1	152	148
3	-2	307	299	6	-1	285	279	-7	-5	251	254	-4	0	250	268
3	-1	474	462	6	0	316	305	-7	-4	271	258	-4	1	430	411
3	0	441	436	6	1	285	278	-7	-3	181	188	-4	2	455	455
3	1	392	375	6	2	238	256	-7	-1	174	166	-4	3	343	376
3	2	424	417	6	3	364	358	-7	0	344	329	-4	4	346	371
3	3	401	386	6	4	312	324	-7	1	340	343	-4	5	356	348
3	4	503	504	6	5	241	237	-7	2	235	238	-4	6	307	326
3	5	378	376	7	-9	143	135	-7	3	210	208	-4	7	364	370
3	6	260	258	7	-8	192	190	-7	4	237	207	-4	8	388	387
3	7	252	257	7	-7	263	249	-7	5	313	302	-4	9	291	290

K	L	FOBS	FCAL
**H =	8****		
-3	-10	208	212
-3	-9	249	260
-3	-8	343	345
-3	-7	321	306
-3	-6	272	269
-3	-5	333	332
-3	-4	391	372
-3	-3	352	338
-3	-2	151	140
-3	-1	81	54
-3	0	280	288
-3	1	456	456
-3	2	405	400
-3	3	317	318
-3	4	217	198
-3	5	291	297
-3	6	381	366
-3	7	324	333
-3	8	291	278
-3	9	264	268
-3	10	222	217
-2	-10	179	177
-2	-9	289	278
-2	-8	393	395
-2	-7	369	362
-2	-6	325	314
-2	-5	304	309
-2	-4	397	389
-2	-3	233	237
-2	-2	328	316
-2	-1	320	309
-2	0	265	265
-2	1	366	398
-2	2	344	339
-2	3	412	419
-2	4	317	318
-2	5	331	329
-2	6	383	410
-2	7	326	322
-2	8	274	273
-2	9	199	185
-1	-10	211	216
-1	-9	315	316
-1	-8	393	381
-1	-7	399	406
-1	-6	300	285
-1	-5	269	256
-1	-4	355	330
-1	-3	378	369
-1	-2	392	387
-1	-1	405	368
-1	0	300	291
-1	1	249	246
-1	2	253	265
-1	3	390	379
-1	4	451	456
-1	5	261	247
-1	6	276	272
-1	7	306	321
-1	8	274	258
-1	9	232	234
0	-11	209	219
0	-10	266	255
0	-9	287	294
0	-8	418	416
0	-7	410	396
0	-6	233	227
0	-5	238	223
0	-4	446	432
0	-3	595	584
0	-2	585	569
0	-1	311	336
0	0	82	55
0	1	192	188
0	2	285	289
0	3	394	370
0	4	351	354
0	5	290	295
0	6	281	272
0	7	245	240
0	8	306	301
0	9	276	285
1	-11	235	232
1	-10	257	257
1	-9	326	328
1	-8	357	351
1	-7	404	400
1	-6	344	348
1	-5	180	171
1	-4	283	286
1	-3	444	443
1	-2	397	395
1	-1	91	81
1	0	88	106
1	1	195	186
1	2	414	389
1	3	401	380
1	4	256	251
1	5	283	278
1	6	312	300
1	7	280	278
1	8	311	303
2	-11	204	191
2	-10	203	212
2	-9	299	302
2	-8	291	289
2	-7	352	355
2	-6	400	393
2	-5	258	277
2	-4	342	347
2	-3	338	337
2	-2	294	303
2	-1	288	282
2	0	182	167
2	1	275	286
2	2	416	391
2	3	340	317
2	4	206	212
2	5	283	270
2	6	281	262
2	7	298	308
2	8	334	325
3	-11	189	190
3	-10	191	198
3	-9	291	282
3	-8	393	386
3	-7	403	401
3	-6	424	433
3	-5	302	329
3	-4	251	275
3	-3	238	241
3	-2	281	279
3	-1	305	301
3	0	249	256
3	1	148	151
3	2	185	186
3	3	224	219
3	4	276	271
3	5	252	255
3	6	258	253
3	7	279	277
4	-10	252	256
4	-9	288	298
4	-8	385	379
4	-7	523	501
4	-6	431	416
4	-5	262	261
4	-4	251	240
4	-3	366	342
4	-2	414	405
4	-1	433	423
4	0	282	274
4	1	158	154
4	2	153	163
4	3	293	298
4	4	188	211
4	5	239	242
4	6	188	181
5	-10	206	212
5	-9	255	263
5	-8	274	282
5	-7	294	291
5	-6	266	267
5	-5	258	254
5	-4	234	249
5	-3	329	317
5	-2	346	337
5	-1	299	291
5	0	204	204
5	1	145	139
5	2	326	321
5	3	366	358
5	4	323	329
5	5	213	209
6	-9	244	244
6	-8	248	236
6	-7	261	258
6	-6	279	278
6	-5	288	294
6	-4	269	267
6	-3	232	232
6	-2	132	139
6	-1	207	215
6	0	248	262
6	1	180	169
6	2	202	205
6	3	247	256
6	4	211	227
7	-8	223	220
7	-7	305	307
7	-6	362	355
7	-5	349	336
7	-4	271	259
7	-3	146	136
7	-2	160	159
7	-1	226	224
7	0	254	261
7	1	171	166
7	2	95	95
8	-6	292	290
8	-5	289	288
8	-4	150	155
8	-3	76	67
8	-2	205	205
8	-1	214	224
**H =	9****		
-9	-1	153	141
-9	0	94	90
-9	1	128	128
-9	2	147	157
-9	3	148	144
-9	4	179	176
-8	-4	240	246
-8	-3	157	172
-8	-2	156	160
-8	-1	198	206
-8	0	222	220
-8	1	214	212
-8	2	214	205
-8	3	167	165
-8	4	134	138
-8	5	153	150
-8	6	258	261
-7	-5	268	267
-7	-4	239	241
-7	-3	235	223
-7	-2	193	184

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
H = 9**				-4	7	247	257	-1	7	288	283	2	7	221	229
-7	-1	289	291	-4	8	295	291	-1	8	260	249	3	-10	184	187
-7	0	327	329	-4	9	245	250	0	-10	233	237	3	-9	273	273
-7	1	266	257	-3	-9	258	268	0	-9	310	311	3	-8	428	422
-7	2	230	219	-3	-8	358	371	0	-8	308	313	3	-7	425	422
-7	3	160	146	-3	-7	324	329	0	-7	321	312	3	-6	471	480
-7	4	138	149	-3	-6	342	336	0	-6	308	297	3	-5	340	334
-7	5	197	205	-3	-5	498	500	0	-5	361	366	3	-4	322	330
-7	6	230	230	-3	-4	559	533	0	-4	447	437	3	-3	467	451
-7	7	275	281	-3	-3	433	422	0	-3	526	534	3	-2	488	485
-6	-6	282	286	-3	-2	279	265	0	-2	447	434	3	-1	350	330
-6	-5	270	264	-3	-1	162	188	0	-1	261	250	3	0	239	229
-6	-4	262	270	-3	0	215	223	0	0	99	101	3	1	223	209
-6	-3	309	300	-3	1	393	396	0	1	263	255	3	2	209	205
-6	-2	274	274	-3	2	354	348	0	2	207	205	3	3	186	182
-6	-1	245	252	-3	3	270	278	0	3	199	207	3	4	341	329
-6	0	283	308	-3	4	125	132	0	4	349	339	3	5	277	262
-6	1	237	216	-3	5	135	143	0	5	303	284	3	6	180	186
-6	2	255	240	-3	6	224	240	0	6	185	183	4	-10	187	183
-6	3	260	242	-3	7	238	226	0	7	227	217	4	-9	219	226
-6	4	242	234	-3	8	261	249	0	8	247	249	4	-8	303	302
-6	5	181	188	-3	9	209	202	1	-10	265	268	4	-7	453	472
-6	6	260	267	-2	-9	270	273	1	-9	297	302	4	-6	363	386
-6	7	244	243	-2	-8	386	375	1	-8	293	287	4	-5	270	283
-6	8	206	199	-2	-7	341	335	1	-7	379	352	4	-4	313	306
-5	-8	221	217	-2	-6	363	348	1	-6	400	403	4	-3	409	402
-5	-7	241	240	-2	-5	431	418	1	-5	293	286	4	-2	457	438
-5	-6	252	235	-2	-4	427	426	1	-4	436	448	4	-1	359	355
-5	-5	299	298	-2	-3	281	257	1	-3	438	437	4	0	216	222
-5	-4	348	353	-2	-2	284	287	1	-2	373	374	4	1	186	181
-5	-3	287	289	-2	-1	322	321	1	-1	144	152	4	2	203	198
-5	-2	268	260	-2	0	202	192	1	0	183	186	4	3	313	315
-5	-1	333	318	-2	1	289	291	1	1	354	336	4	4	285	275
-5	0	232	237	-2	2	373	355	1	2	327	325	4	5	255	253
-5	1	130	159	-2	3	332	320	1	3	241	244	5	-9	202	193
-5	2	240	245	-2	4	194	194	1	4	285	260	5	-8	265	263
-5	3	345	349	-2	5	220	223	1	5	268	253	5	-7	324	325
-5	4	188	175	-2	6	341	340	1	6	224	221	5	-6	293	303
-5	5	285	291	-2	7	296	286	1	7	182	181	5	-5	252	252
-5	6	269	280	-2	8	262	256	1	8	250	241	5	-4	223	240
-5	7	266	264	-2	9	160	168	2	-10	184	185	5	-3	300	299
-5	8	264	267	-1	-10	215	218	2	-9	273	277	5	-2	336	353
-4	-8	308	311	-1	-9	319	314	2	-8	319	315	5	-1	249	241
-4	-7	251	249	-1	-8	372	361	2	-7	383	389	5	0	171	198
-4	-6	286	292	-1	-7	348	348	2	-6	391	384	5	1	144	136
-4	-5	408	405	-1	-6	380	363	2	-5	385	389	5	2	198	209
-4	-4	513	501	-1	-5	377	381	2	-4	290	281	5	3	264	272
-4	-3	356	326	-1	-4	396	403	2	-3	341	360	5	4	256	258
-4	-2	230	213	-1	-3	358	353	2	-2	431	426	6	-8	265	252
-4	-1	141	137	-1	-2	369	353	2	-1	275	283	6	-7	310	296
-4	0	154	164	-1	0	190	188	2	0	188	198	6	-6	327	314
-4	1	186	193	-1	1	224	210	2	1	449	433	6	-5	336	323
-4	2	247	251	-1	2	338	337	2	2	310	295	6	-4	325	317
-4	3	250	227	-1	3	231	232	2	3	164	176	6	-3	366	356
-4	4	179	162	-1	4	249	253	2	4	231	234	6	-2	260	239
-4	5	128	128	-1	5	220	203	2	5	328	312	6	-1	239	231
-4	6	200	193	-1	6	277	264	2	6	178	187	6	0	280	281

Table 30. Continued

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
H = 9**				-5	6	211	222	-1	-6	222	225	2	0	404	383
6	1	177	181	-5	7	206	211	-1	-5	384	377	2	1	376	370
6	2	143	141	-4	-8	182	187	-1	-4	417	416	2	2	317	332
6	3	203	216	-4	-7	166	166	-1	-3	474	450	2	3	222	205
7	-6	324	326	-4	-6	298	291	-1	-2	422	423	2	4	266	241
7	-5	281	271	-4	-5	435	433	-1	-1	383	403	2	5	222	230
7	-4	277	282	-4	-4	405	409	-1	0	314	319	2	6	168	155
7	-3	231	235	-4	-3	324	338	-1	1	292	296	3	-9	225	228
7	-2	226	231	-4	-2	383	392	-1	2	394	381	3	-8	283	284
7	-1	191	198	-4	-1	388	364	-1	3	383	356	3	-7	250	240
7	0	243	251	-4	0	390	371	-1	4	319	320	3	-6	262	280
H = 10**				-4	1	422	425	-1	5	240	232	3	-5	209	209
-8	-2	229	230	-4	2	332	343	-1	6	208	205	3	-4	293	298
-8	-1	330	327	-4	3	239	247	-1	7	170	193	3	-3	394	398
-8	0	301	293	-4	4	145	155	0	-9	232	230	3	-2	436	443
-8	1	198	205	-4	5	111	103	0	-8	201	205	3	-1	439	441
-8	2	188	202	-4	6	149	160	0	-7	204	212	3	0	391	388
-8	3	159	157	-4	7	239	238	0	-6	303	305	3	1	313	307
-8	4	136	133	-4	8	191	181	0	-5	430	433	3	2	228	224
-7	-4	260	269	-3	-8	208	211	0	-4	491	484	3	3	288	272
-7	-3	280	281	-3	-7	177	170	0	-3	566	576	3	4	255	253
-7	-2	273	272	-3	-6	302	296	0	-2	402	392	3	5	191	193
-7	-1	356	351	-3	-5	454	446	0	-1	276	287	4	-8	211	227
-7	0	381	367	-3	-4	385	376	0	0	364	349	4	-7	240	235
-7	1	266	253	-3	-3	340	321	0	1	388	366	4	-6	195	186
-7	2	173	176	-3	-2	357	349	0	2	411	379	4	-5	163	172
-7	3	78	90	-3	-1	381	381	0	3	340	311	4	-4	308	315
-7	4	166	164	-3	0	336	348	0	4	249	246	4	-3	445	438
-7	5	170	172	-3	1	436	458	0	5	145	154	4	-2	403	412
-7	6	154	143	-3	2	360	367	0	6	113	109	4	-1	309	325
-6	-6	251	264	-3	3	248	255	0	7	159	153	4	0	244	238
-6	-5	235	243	-3	4	227	223	1	-9	241	226	4	1	157	173
-6	-4	273	276	-3	5	141	137	1	-8	178	184	4	2	189	199
-6	-3	336	323	-3	6	200	197	1	-7	296	280	4	3	213	235
-6	-2	340	336	-3	7	209	214	1	-6	384	378	4	4	200	209
-6	-1	242	250	-3	8	224	228	1	-5	276	276	5	-8	222	225
-6	0	301	313	-2	-9	228	245	1	-4	459	476	5	-7	208	206
-6	1	280	271	-2	-8	260	252	1	-3	451	456	5	-6	249	235
-6	2	207	207	-2	-7	246	247	1	-2	390	415	5	-5	290	275
-6	3	186	190	-2	-6	249	256	1	-1	387	377	5	-4	323	309
-6	4	138	153	-2	-5	345	335	1	0	426	402	5	-3	358	346
-6	5	169	163	-2	-4	348	336	1	1	453	442	5	-2	318	313
-6	6	189	192	-2	-3	284	288	1	2	327	320	5	-1	241	231
-6	7	192	191	-2	-2	367	355	1	3	261	255	5	0	218	211
-5	-7	199	200	-2	-1	402	419	1	4	186	179	5	1	200	200
-5	-6	233	242	-2	0	334	333	1	5	165	168	5	2	228	241
-5	-5	286	281	-2	1	321	314	1	6	170	181	5	3	278	270
-5	-4	316	307	-2	2	317	304	1	7	176	179	6	-6	225	234
-5	-3	297	298	-2	3	303	300	2	-9	226	221	6	-5	263	260
-5	-2	281	291	-2	4	259	248	2	-8	236	230	6	-4	277	282
-5	-1	257	261	-2	5	232	204	2	-7	255	254	6	-3	261	265
-5	0	213	213	-2	6	290	293	2	-6	337	312	6	-2	245	244
-5	1	275	260	-2	7	216	215	2	-5	350	361	6	-1	252	250
-5	2	299	271	-2	8	199	203	2	-4	314	309	6	0	251	258
-5	3	218	226	-1	-9	230	229	2	-3	359	358	6	1	217	220
-5	4	151	150	-1	-8	253	245	2	-2	401	392	**H = 11****			
-5	5	142	165	-1	-7	165	169	2	-1	405	412	-7	-2	229	237

Table 30. Continued

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
H = 11**				-2	-7	205	204	1	5	201	206	-5	2	266	272
-7	-1	347	341	-2	-6	200	202	2	-8	161	161	-5	3	232	258
-7	0	434	433	-2	-5	247	246	2	-7	130	139	-5	4	263	271
-7	1	272	270	-2	-4	278	274	2	-6	219	211	-4	-5	239	251
-7	2	141	153	-2	-3	281	278	2	-5	230	233	-4	-4	205	196
-7	3	137	132	-2	-2	322	311	2	-4	208	204	-4	-3	168	161
-7	4	198	204	-2	-1	459	448	2	-3	230	255	-4	-2	137	132
-6	-4	203	214	-2	0	416	436	2	-2	220	241	-4	-1	190	201
-6	-3	285	296	-2	1	336	344	2	-1	319	319	-4	0	283	296
-6	-2	300	298	-2	2	321	337	2	0	296	294	-4	1	315	312
-6	-1	326	306	-2	3	318	310	2	1	366	348	-4	2	307	308
-6	0	388	369	-2	4	296	291	2	2	383	362	-4	3	247	248
-6	1	259	262	-2	5	186	194	2	3	261	248	-4	4	256	264
-6	2	149	161	-2	6	230	231	2	4	230	227	-4	5	248	244
-6	3	189	205	-1	-8	189	189	3	-8	199	197	-3	-6	165	172
-6	4	231	218	-1	-7	161	154	3	-7	136	134	-3	-5	237	231
-6	5	235	240	-1	-6	107	120	3	-6	119	134	-3	-4	213	210
-5	-5	216	222	-1	-5	268	255	3	-5	163	164	-3	-3	140	143
-5	-4	326	317	-1	-4	371	358	3	-4	227	233	-3	-2	124	139
-5	-3	362	356	-1	-3	386	378	3	-3	247	245	-3	-1	237	242
-5	-2	298	306	-1	-2	405	386	3	-2	273	275	-3	0	314	322
-5	-1	290	288	-1	-1	383	386	3	-1	361	366	-3	1	345	356
-5	0	310	300	-1	0	402	393	3	0	326	337	-3	2	309	296
-5	1	309	318	-1	1	338	331	3	1	258	278	-3	3	228	231
-5	2	293	301	-1	2	331	346	3	2	308	303	-3	4	201	203
-5	3	333	322	-1	3	320	308	3	3	264	276	-3	5	257	258
-5	4	265	261	-1	4	278	271	3	4	173	186	-2	-6	172	164
-5	5	218	210	-1	5	178	183	4	-7	121	115	-2	-5	165	161
-5	6	212	221	-1	6	205	195	4	-6	61	73	-2	-4	167	165
-4	-6	210	221	0	-8	173	170	4	-5	131	139	-2	-3	158	166
-4	-5	336	326	0	-7	123	129	4	-4	260	248	-2	-2	221	209
-4	-4	320	304	0	-6	114	112	4	-3	330	320	-2	-1	275	258
-4	-3	298	289	0	-5	293	293	4	-2	328	320	-2	0	283	294
-4	-2	226	247	0	-4	497	490	4	-1	306	296	-2	1	267	275
-4	-1	328	336	0	-3	524	521	4	0	247	253	-2	2	320	321
-4	0	513	500	0	-2	359	357	4	1	251	253	-2	3	231	225
-4	1	453	460	0	-1	278	276	4	2	270	265	-2	4	261	260
-4	2	398	408	0	0	303	294	5	-6	93	100	-2	5	292	278
-4	3	313	321	0	1	331	338	5	-5	163	169	-1	-7	156	153
-4	4	230	231	0	2	356	353	5	-4	232	236	-1	-6	140	129
-4	5	142	151	0	3	323	309	5	-3	243	263	-1	-5	179	190
-4	6	202	203	0	4	237	242	5	-2	213	231	-1	-4	210	205
-3	-7	143	146	0	5	199	196	5	-1	225	226	-1	-3	241	240
-3	-6	251	251	0	6	166	168	5	0	227	220	-1	-2	255	253
-3	-5	313	308	1	-8	119	118	**H = 12****				-1	-1	228	230
-3	-4	286	291	1	-7	125	145	-6	-2	208	209	-1	0	214	226
-3	-3	233	241	1	-6	176	179	-6	-1	268	273	-1	1	286	300
-3	-2	276	263	1	-5	211	192	-6	0	296	295	-1	2	315	313
-3	-1	463	452	1	-4	380	386	-6	1	293	287	-1	3	279	265
-3	0	454	453	1	-3	368	362	-6	2	237	227	-1	4	270	266
-3	1	416	434	1	-2	271	275	-6	3	233	236	-1	5	239	242
-3	2	286	299	1	-1	213	226	-5	-4	190	196	0	-7	117	108
-3	3	231	226	1	0	288	290	-5	-3	163	168	0	-6	91	92
-3	4	213	209	1	1	384	368	-5	-2	221	227	0	-5	151	143
-3	5	157	166	1	2	419	388	-5	-1	243	236	0	-4	323	319
-3	6	195	199	1	3	296	290	-5	0	260	260	0	-3	231	250
-2	-8	131	132	1	4	201	186	-5	1	272	280	0	-2	133	143

Table 30. Continued

K	L	FOBS	FCAL
H = 12**			
0	-1	118	116
0	0	216	220
0	1	303	289
0	2	347	337
0	3	298	292
0	4	236	225
1	-7	125	128
1	-6	110	107
1	-5	128	136
1	-4	206	212
1	-3	190	189
1	-2	109	120
1	-1	139	149
1	0	262	243
1	1	366	354
1	2	310	308
1	3	222	222
1	4	188	183
2	-6	171	171
2	-5	130	132
2	-4	133	135
2	-3	222	215
2	-2	235	213
2	-1	213	216
2	0	285	281
2	1	288	282
2	2	240	259
2	3	222	223
3	-6	94	96
3	-5	117	125
3	-4	167	164
3	-3	231	227
3	-2	207	196
3	-1	194	201
3	0	176	172
3	1	192	186
4	-4	163	175
4	-3	199	204
4	-2	221	217
4	-1	136	147
H = 13**			
-4	-2	74	78
-4	-1	114	122
-4	0	219	225
-4	1	256	261
-4	2	179	195
-3	-4	117	119
-3	-3	60	74
-3	-2	75	83
-3	-1	133	141
-3	0	251	246
-3	1	264	267
-3	2	191	194
-2	-4	131	143
-2	-3	126	123
-2	-2	147	160
-2	-1	144	143
-2	0	195	199
-2	1	235	222
-2	2	221	238
-2	3	197	193
-1	-5	172	186
-1	-4	141	139
-1	-3	165	176
-1	-2	131	133
-1	-1	80	91
-1	0	162	151
-1	1	238	234
-1	2	251	243
0	-5	138	148
0	-4	220	244
0	-3	161	159
0	-2	72	68
0	-1	108	104
0	0	153	153
0	1	222	211
0	2	228	228
1	-4	198	184
1	-3	192	198
1	-2	168	158
1	-1	148	153
1	0	178	179
1	1	221	230
2	-3	188	185
2	-2	158	171